# 5. Phase analysis and lattice parameter determination

# Contents

## **5.1** Qualitative analysis

- Fundamental

X-ray diffraction analysis is based on crystal structure. Each crystalline material has its specific structural parameters, including lattice type, number and position of atoms in the unit cell, and unit cell size, etc.

These structural parameters must be reflected in the X-ray diffraction pattern.

The number, position and intensity of the diffraction lines of a polycrystalline material are characteristics of the material and can therefore be used as a marker to identify the phase of the material.

There are no two substances with exactly the same diffraction pattern in the world, so the diffraction pattern can be compared with the standard material diffraction card for phase identification.

The position of the diffraction line is determined by $2\theta$, which depends on the wavelength $\lambda$ and the interplanar spacing $d$, where $d$ is the basic quantity determined by the crystal structure. When applying, compare the pattern to be tested with the standard pattern $d$ and $I$ series to determine the physical phase.

## **5.1** Qualitative analysis

- Powder Diffraction Card (PDF)

Powder diffraction cards are indispensable data for qualitative phase analysis. The card has gone through several stages since its publication.

1. Published by ASTM since 1941.
2. Published by the Joint Committee on Powder Diffraction Standards JCPDF in 1969.
3. Since 1978, JCPDF has been jointly published with the International Center for Diffraction Data, namely JCPDF/ICDD.
4. Cards after 1992 were published uniformly by ICDD. By 1997, there were 47 sets of cards, including about 67,000 organic and inorganic items.

Figure (page 5) is the 46th set of PDF (ICDD) cards published in 1996. The content of each column in the card is shown in the description of page 6.

# **5.1** Qualitative analysis

- Powder Diffraction Card (PDF)

46-394 ★

$SmAlO_3$
Aluminum Samarium Oxide

Rad. CuK$_{\alpha1}$ λ1.540598 Filter Ge Mono. D-sp Guinier Cut off 3.9
Int. Densitometer $I / I_{cor}$ . 3.44
Ref. Wang, P. Shanghai Inst. Of Ceramics, Chinese Academy of Sciences, Shanghai, china, ICDD Grant-in-Aid, (1994)

Sys. Tetragonal S.G.
*a* 5.2876(2) *b* *c* 7.4858(7) *A* *C* 1.4157
*α* *β* *γ* *Z*4 *mp*
Ref. Ibid. $D_x$ 7.153 $D_m$ SS/FOM $F_{19}$ = 39 (.007,71)

Integrated in tensities, Prepared by heating compact powder mixtuer of $Sm_2O_3$ and $Al_2O_3$ according to the stoichiometric ratio of $SmAlO_3$ at 1500C in molybdenum silicide-resistance furnace in air for 2days, Silicon used as internal standard. To replace 9-82 and 29-83.

| *d* /Å | *Int* | *hkl* |
|---|---|---|
| 3.737 | 62 | 110 |
| 3.345 | 5 | 111 |
| 2.645 | 100 | 112 |
| 2.4948 | 4 | 003 |
| 2.2549 | 2 | 211 |
| 2.1593 | 46 | 202 |
| 1.8701 | 62 | 220 |
| 1.8149 | 6 | 203 |
| 1.6727 | 41 | 222 |
| 1.6320 | 7 | 311 |
| 1.5265 | 49 | 312 |
| 1.3900 | 6 | 115 |
| 1.3220 | 33 | 400 |
| 1.3025 | 1 | 205 |
| 1.2462 | 19 | 330 |
| 1.1822 | 18 | 420 |
| 1.1677 | 5 | 421 |

Diffraction card of $SmAlO_3$ powder

# **5.1** Qualitative analysis

- Powder Diffraction Card (PDF)

1. Column 1 is the chemical formula and name of the substance.

2. Column 2 is the experimental conditions for obtaining diffraction data.

3. Column 3 is the crystallographic data for the substance.

46-394 ★

$SmAlO_3$
Aluminum Samarium Oxide

Rad. $CuK_{\alpha 1}$ λ1.540598 Filter Ge Mono. D-sp Guinier Cut off 3.9
Int. Densitometer $I/I_{cor}$. 3.44
Ref. Wang, P. Shanghai Inst. Of Ceramics, Chinese Academy of Sciences, Shanghai, china, ICDD Grant-in-Aid, (1994)

Sys. Tetragonal S.G.
$a$ 5.2876(2) $b$ $c$ 7.4858(7) $A$ $C$ 1.4157
$\alpha$ $\beta$ $\gamma$ Z4 $mp$
Ref. Ibid. $D_x$ 7.153 $D_m$ SS/FOM $F_{19}$ = 39 (.007,71)

Integrated in tensities, Prepared by heating compact powder mixtuer of $Sm_2O_3$ and $Al_2O_3$ according to the stoichiometric ratio of $SmAlO_3$ at 1500C in molybdenum silicide-resistance furnace in air for 2days, Silicon used as internal standard. To replace 9-82 and 29-83.

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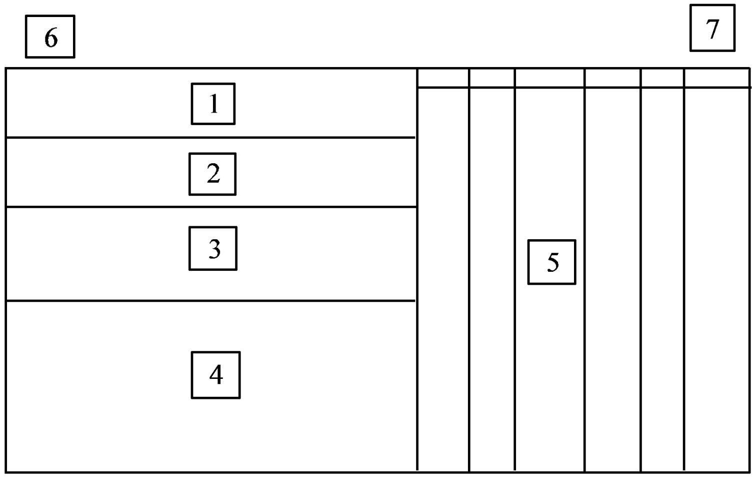
| 1.3220 | 33 | 400 |
| 1.3025 | 1 | 205 |
| 1.2462 | 19 | 330 |
| 1.1822 | 18 | 420 |
| 1.1677 | 5 | 421 |

4. Column 4 contains data such as sample source, preparation and chemical analysis, as well as the temperature at which the data was obtained, and card replacement instructions, etc.



5. Column 5 is the interplanar spacing, diffraction intensity and corresponding crystal plane index of the substance.

6. Column 6 is the card number.

7. Column 7 is the quality mark of the card.

## **5.1** Qualitative analysis

- Index

The card file index can be divided into two categories according to the substance: organic phase and inorganic phase; according to the search method, it can be divided into two types: alphabetical index and numerical (Hanawalt) index.

1. alphabetical index

Arranged by the English name of the substance. The mass mark, substance name, chemical formula, $d$ value and relative intensity of the three strong diffraction lines of the card in each row, and card serial number.

2. numerical index

The numerical (Hanawalt) index is grouped by the $d_1$ value of the strongest line, and the $d_1$ values are arranged from large to small. Within each group, the $d_2$ values of the next strongest lines are arranged in the order of decreasing, and the columns with the same $d_2$ value are arranged in decreasing order of $d_1$ value. arranged in order. The entries list the card quality mark, the $d$ value and intensity of the eight strongest lines, chemical formula, card number, etc.

The order of the three strong lines in a diffraction pattern often changes due to various factors.

## **5.1** Qualitative analysis

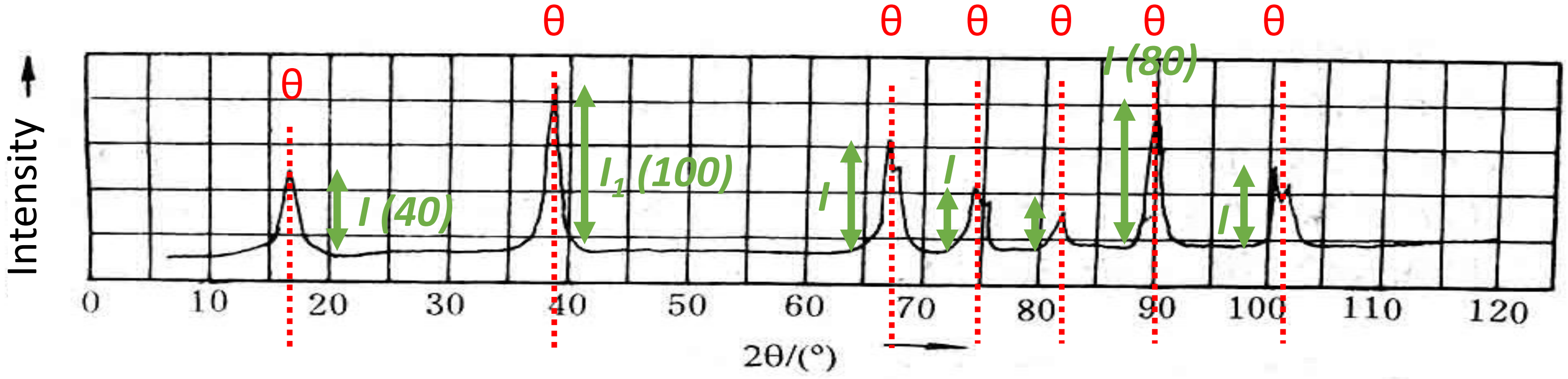
- Process overview
- Measurement of interplanar spacing ***d***: Qualitative phase analysis does not have very high requirements for the ***d*** value. Take the apex or midline position of the diffraction peak in the diffraction pattern as the **2θ** value of the line (accurate to 0.01°) and use the reference book to find out (or use Bragg's law to calculate) the corresponding ***d*** value.
- For the measurement of relative intensity $I/I_1$, it is customary to measure only the peak height and not the integrated area. The peak height allows for a rough estimate without precise measurement. Set the intensity of the highest peak ($I_1$) to 100 and determine the relative intensities of the other peaks accordingly.

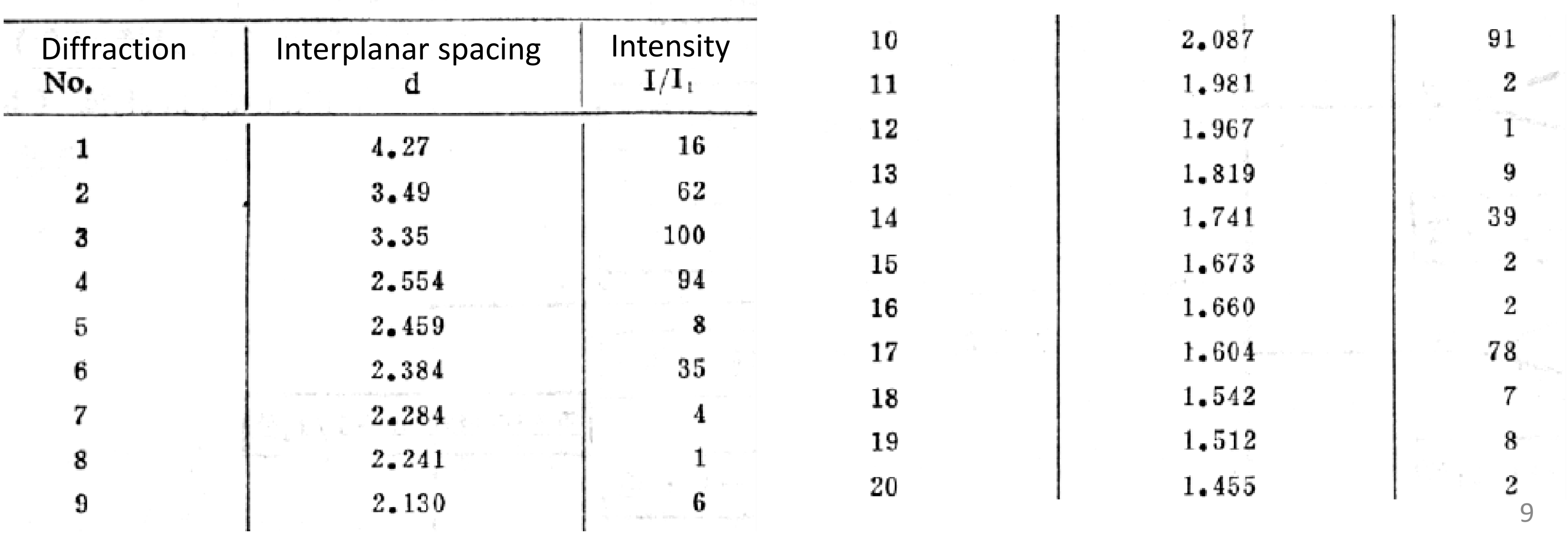
Current X-ray diffractometers generally automatically output the ***d*** and ***I*** value tables corresponding to each diffraction peak through data collection and processing.

when the ***d*** series and the corresponding $I/I_1$ are obtained according to the decreasing plane distance, the physical phase identification is carried out according to the following procedures.

# **5.1** Qualitative analysis

- Process overview





| Diffraction No. | Interplanar spacing d | Intensity $I/I_1$ |
|---|---|---|
| 1 | 4.27 | 16 |
| 2 | 3.49 | 62 |
| 3 | 3.35 | 100 |
| 4 | 2.554 | 94 |
| 5 | 2.459 | 8 |
| 6 | 2.384 | 35 |
| 7 | 2.284 | 4 |
| 8 | 2.241 | 1 |
| 9 | 2.130 | 6 |
| 10 | 2.087 | 91 |
| 11 | 1.981 | 2 |
| 12 | 1.967 | 1 |
| 13 | 1.819 | 9 |
| 14 | 1.741 | 39 |
| 15 | 1.673 | 2 |
| 16 | 1.660 | 2 |
| 17 | 1.604 | 78 |
| 18 | 1.542 | 7 |
| 19 | 1.512 | 8 |
| 20 | 1.455 | 2 |

## **5.1** Qualitative analysis

- Process overview

1. Select the three diffraction lines with the highest intensity and arrange their ***d*** values in order of decreasing intensity, followed by the others in order of decreasing intensity.

2. Find the corresponding $d_1$ (face distance of the strongest line) group in the index.

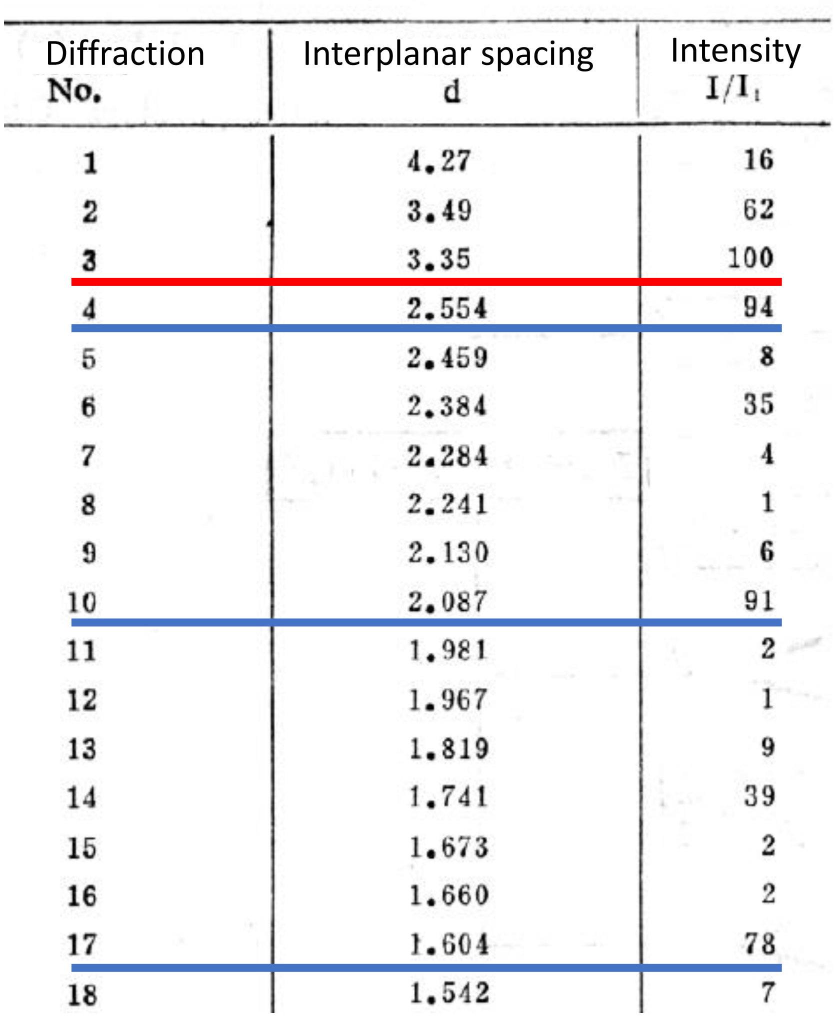
3. Press $d_2$ of the sub-strong line to find the closest lines. The rows in the same group are arranged in descending order of $d_2$, which is very important for searching.

4. Find the data that is close to $d_1$ and $d_2$, and then check the 3rd , 4th , and 8th strong lines in order to determine the most likely physical phase and its card number.

5. Select the card and carefully compare the experimental values of ***d*** and $I/I_1$ with the data on the card. If the two data correspond well, the physical phase can be determined.

## **5.1** Qualitative analysis

- Process overview



| Diffraction No. | Interplanar spacing d | Intensity $I/I_1$ |
|---|---|---|
| 1 | 4.27 | 16 |
| 2 | 3.49 | 62 |
| 3 | 3.35 | 100 |
| 4 | 2.554 | 94 |
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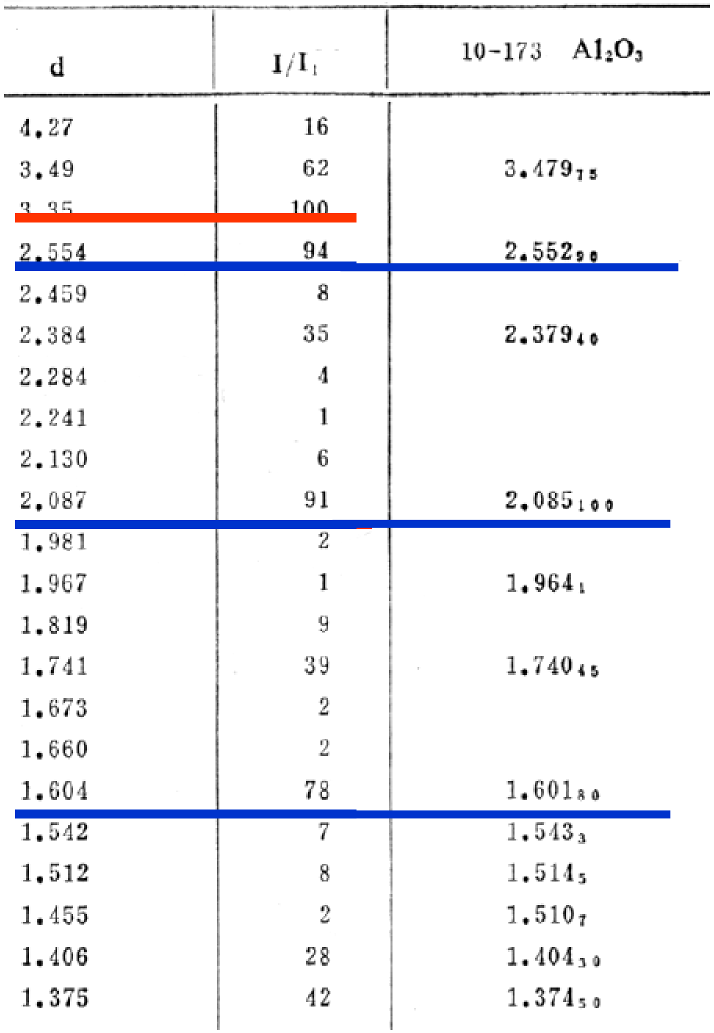
| 13 | 1.819 | 9 |
| 14 | 1.741 | 39 |
| 15 | 1.673 | 2 |
| 16 | 1.660 | 2 |
| 17 | 1.604 | 78 |
| 18 | 1.542 | 7 |

Select 3 strong lines and use numerical index to search in the 3.39~3.32 group in descending order of the second ***d***. The result is not found, indicating that these 3 strongest lines do not belong to the same phase. Select 3 more lines to search. Cards with card numbers 10-173 can be found, $Al_2O_3$.

# **5.1** Qualitative analysis

- Process overview



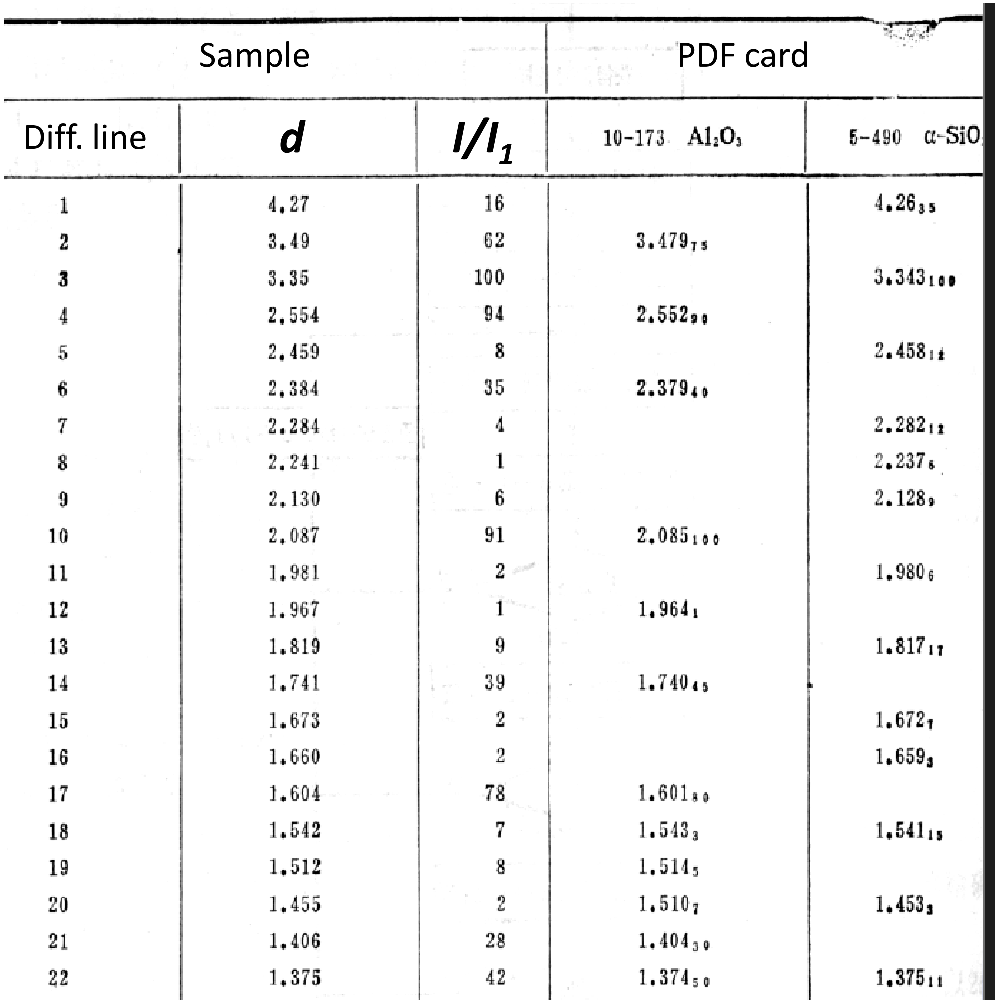
| d | $I/I_1$ | 10-173 $Al_2O_3$ |
|---|---|---|
| 4.27 | 16 | |
| 3.49 | 62 | $3.479_{75}$ |
| 3.35 | 100 | |
| 2.554 | 94 | $2.552_{90}$ |
| 2.459 | 8 | |
| 2.384 | 35 | $2.379_{40}$ |
| 2.284 | 4 | |
| 2.241 | 1 | |
| 2.130 | 6 | |
| 2.087 | 91 | $2.085_{100}$ |
| 1.981 | 2 | |
| 1.967 | 1 | $1.964_{1}$ |
| 1.819 | 9 | |
| 1.741 | 39 | $1.740_{45}$ |
| 1.673 | 2 | |
| 1.660 | 2 | |
| 1.604 | 78 | $1.601_{80}$ |
| 1.542 | 7 | $1.543_{3}$ |
| 1.512 | 8 | $1.514_{5}$ |
| 1.455 | 2 | $1.510_{7}$ |
| 1.406 | 28 | $1.404_{30}$ |
| 1.375 | 42 | $1.374_{50}$ |

Take out the card and compare the data in the card with the diffraction data. It is found that all the data on the card can be found in the diffraction data. Remove these data and the first phase search is completed.

# **5.1** Qualitative analysis

- Process overview

- Renormalize the remaining data, select 3 strong lines to search, and find that the card number is 5-490, α-$SiO_2$.
- Obtain the card for verification and confirm the phase.
- During the verification, it was found that some diffraction lines belong to two phases.
- At this point, there are no remaining diffraction lines and the phase search is completed.



| Sample | | | PDF card | |
|---|---|---|---|---|
| Diff. line | *d* | *$I/I_1$* | 10-173 $Al_2O_3$ | 5-490 α-SiO |
| 1 | 4.27 | 16 | | $4.26_{35}$ |
| 2 | 3.49 | 62 | $3.479_{75}$ | |
| 3 | 3.35 | 100 | | $3.343_{100}$ |
| 4 | 2.554 | 94 | $2.552_{90}$ | |
| 5 | 2.459 | 8 | | $2.458_{12}$ |
| 6 | 2.384 | 35 | $2.379_{40}$ | |
| 7 | 2.284 | 4 | | $2.282_{12}$ |
| 8 | 2.241 | 1 | | $2.237_{6}$ |
| 9 | 2.130 | 6 | | $2.128_{9}$ |
| 10 | 2.087 | 91 | $2.085_{100}$ | |
| 11 | 1.981 | 2 | | $1.980_{6}$ |
| 12 | 1.967 | 1 | $1.964_{1}$ | |
| 13 | 1.819 | 9 | | $1.817_{17}$ |
| 14 | 1.741 | 39 | $1.740_{45}$ | |
| 15 | 1.673 | 2 | | $1.672_{7}$ |
| 16 | 1.660 | 2 | | $1.659_{3}$ |
| 17 | 1.604 | 78 | $1.601_{80}$ | |
| 18 | 1.542 | 7 | $1.543_{3}$ | $1.541_{15}$ |
| 19 | 1.512 | 8 | $1.514_{5}$ | |
| 20 | 1.455 | 2 | $1.510_{7}$ | $1.453_{3}$ |
| 21 | 1.406 | 28 | $1.404_{30}$ | |
| 22 | 1.375 | 42 | $1.374_{50}$ | $1.375_{11}$ |

## **5.1** Qualitative analysis

- Possible problems

- In a mixed sample, the phase with too little content is not enough to produce its own complete diffraction pattern, or even no diffraction lines.

- Due to the preferred orientation of the crystal, only one or two extremely strong diffraction lines may appear in its diffraction pattern, and it is also quite difficult to determine the physical phase.

- Diffraction lines of heterogeneous mixtures may overlap with each other.

- Phases with the same lattice and similar lattice parameters have very similar diffraction patterns, and it is difficult to distinguish them.

## **5.1** Qualitative analysis

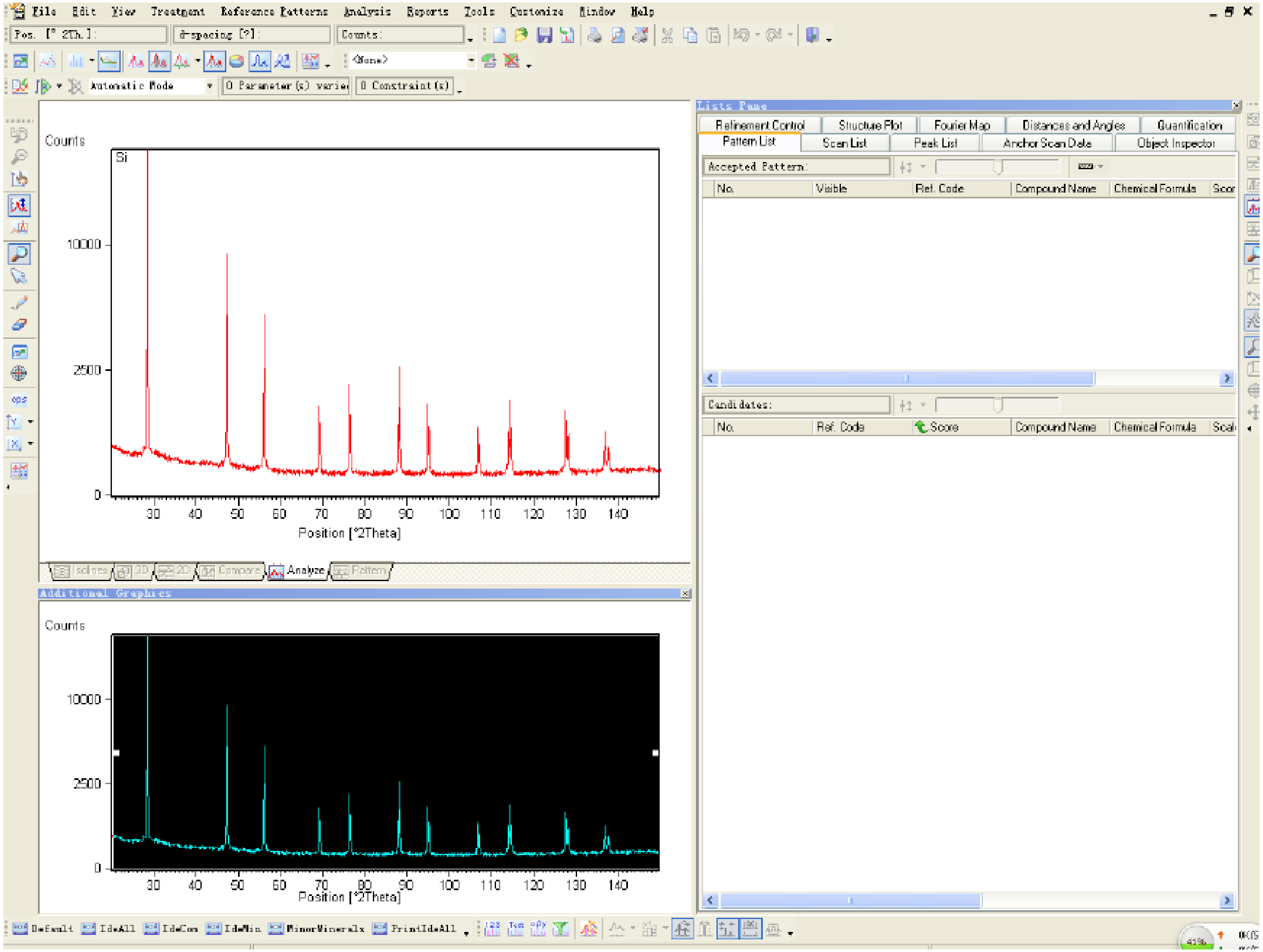
- Automatic search

Phase retrieval is a tedious and time-consuming task. With the development of computer technology, current X-ray diffractometers are equipped with automatic retrieval systems.

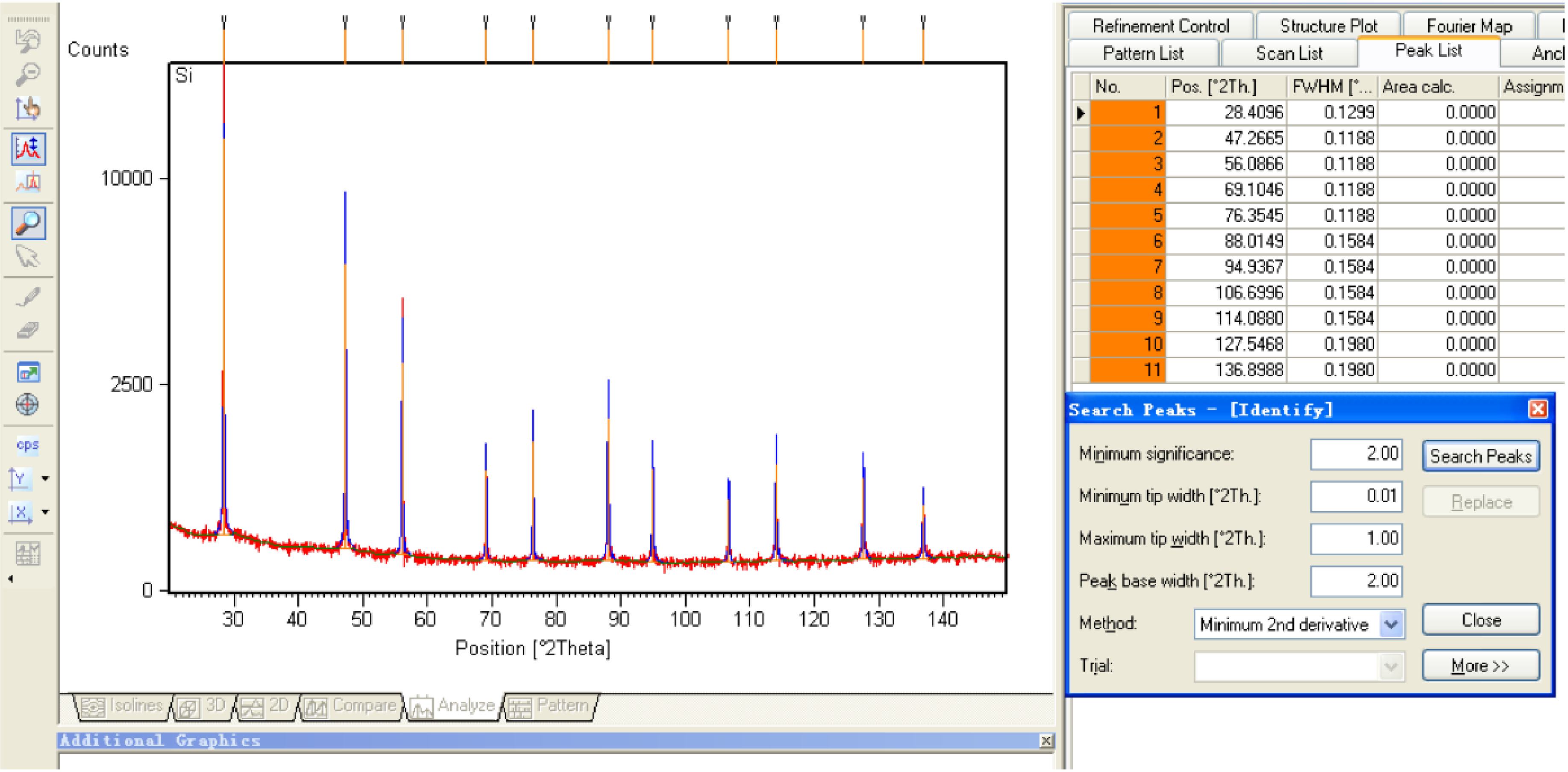
1. Establish a database and input and store the diffraction patterns of standard materials into the computer automatic retrieval system.

2. To search for matches, enter the experimental diffraction data and errors of the sample to be measured. It is also necessary to enter the elemental composition information of the sample and the sub-database type to which the phase belongs (organic, inorganic, metal, mineral, etc.). Computer program matches, searches and selects standard patterns.

## **5.1** Qualitative analysis



# **5.1** Qualitative analysis

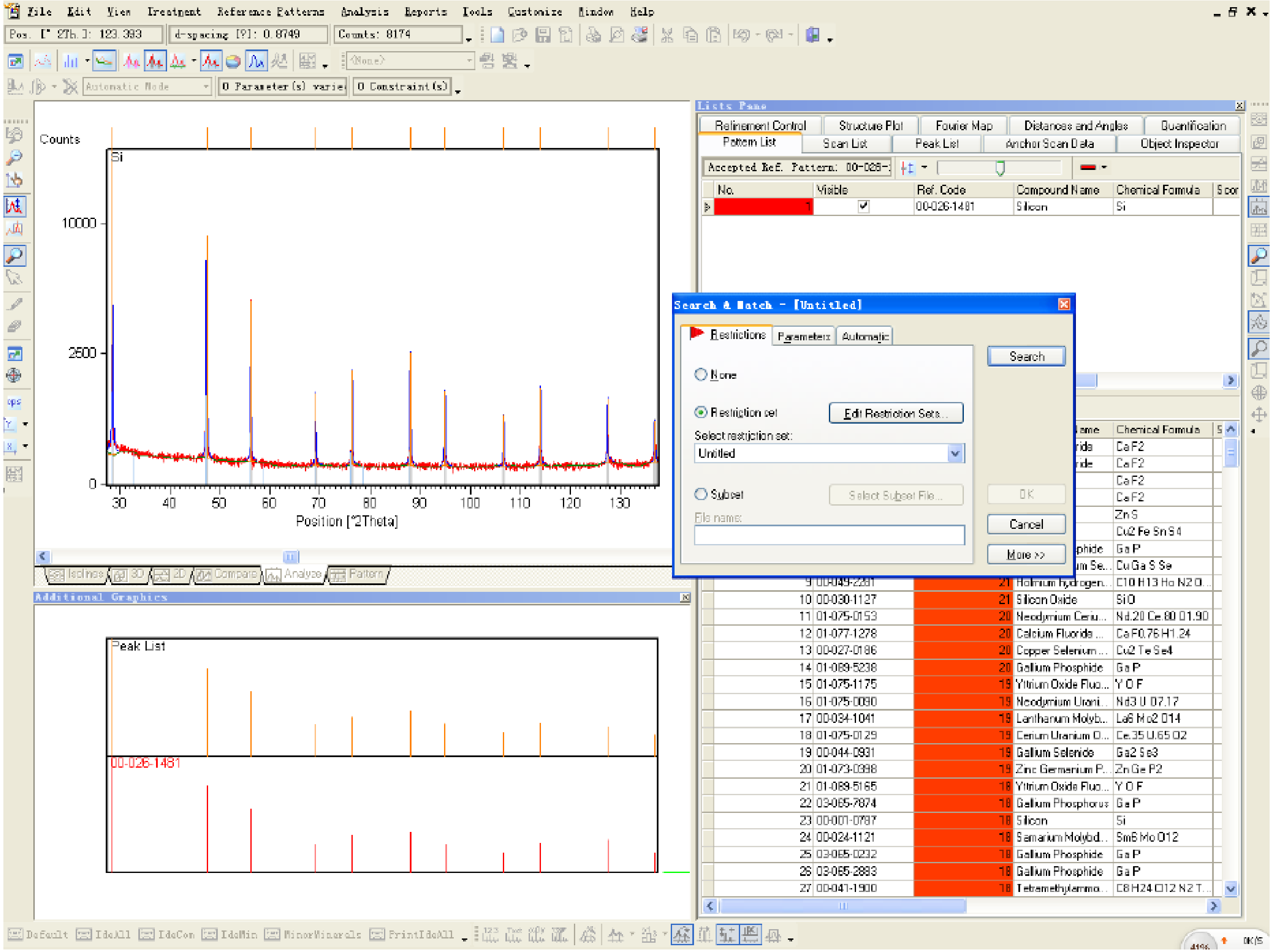


| No. | Pos. [°2Th.] | FWHM [°... | Area calc. | Assignm |
|---|---|---|---|---|
| 1 | 28.4096 | 0.1299 | 0.0000 | |
| 2 | 47.2665 | 0.1188 | 0.0000 | |
| 3 | 56.0866 | 0.1188 | 0.0000 | |
| 4 | 69.1046 | 0.1188 | 0.0000 | |
| 5 | 76.3545 | 0.1188 | 0.0000 | |
| 6 | 88.0149 | 0.1584 | 0.0000 | |
| 7 | 94.9367 | 0.1584 | 0.0000 | |
| 8 | 106.6996 | 0.1584 | 0.0000 | |
| 9 | 114.0880 | 0.1584 | 0.0000 | |
| 10 | 127.5468 | 0.1980 | 0.0000 | |
| 11 | 136.8988 | 0.1980 | 0.0000 | |

**Search Peaks - [Identify]**

Minimum significance: 2.00
Minimum tip width [°2Th.]: 0.01
Maximum tip width [°2Th.]: 1.00
Peak base width [°2Th.]: 2.00
Method: Minimum 2nd derivative
Trial:

# **5.1** Qualitative analysis



Accepted Ref. Pattern: 00-026-1481

| No. | Visible | Ref. Code | Compound Name | Chemical Formula | Scor |
|---|---|---|---|---|---|
| 1 | ☑ | 00-026-1481 | Silicon | Si | |

○ None

● Restriction set

Select restriction set: Untitled

○ Subset

File name:

| | | | ame | Chemical Formula |
|---|---|---|---|---|
| | | | ride | Ca F2 |
| | | | ride | Ca F2 |
| | | | | Ca F2 |
| | | | | Ca F2 |
| | | | | Zn S |
| | | | | Cu2 Fe Sn S4 |
| | | | phide | Ga P |
| | | | um Se... | Cu Ga S Se |
| 9 | 00-049-2281 | 21 | Holmium hydrogen... | C10 H13 Ho N2 O... |
| 10 | 00-030-1127 | 21 | Silicon Oxide | Si O |
| 11 | 01-075-0153 | 20 | Neodymium Ceriu... | Nd.20 Ce.80 O1.90 |
| 12 | 01-077-1278 | 20 | Calcium Fluoride ... | Ca F0.76 H1.24 |
| 13 | 00-027-0186 | 20 | Copper Selenium ... | Cu2 Te Se4 |
| 14 | 01-089-5238 | 20 | Gallium Phosphide | Ga P |
| 15 | 01-075-1175 | 19 | Yttrium Oxide Fluo... | Y O F |
| 16 | 01-075-0090 | 19 | Neodymium Urani... | Nd3 U O7.17 |
| 17 | 00-034-1041 | 19 | Lanthanum Molyb... | La6 Mo2 O14 |
| 18 | 01-075-0129 | 19 | Cerium Uranium O... | Ce.35 U.65 O2 |
| 19 | 00-044-0931 | 19 | Gallium Selenide | Ga2 Se3 |
| 20 | 01-073-0398 | 19 | Zinc Germanium P... | Zn Ge P2 |
| 21 | 01-089-5165 | 18 | Yttrium Oxide Fluo... | Y O F |
| 22 | 03-065-7874 | 18 | Gallium Phosphorus | Ga P |
| 23 | 00-001-0787 | 18 | Silicon | Si |
| 24 | 00-024-1121 | 18 | Samarium Molybd... | Sm6 Mo O12 |
| 25 | 03-065-0232 | 18 | Gallium Phosphide | Ga P |
| 26 | 03-065-2883 | 18 | Gallium Phosphide | Ga P |
| 27 | 00-041-1900 | 18 | Tetramethylammo... | C8 H24 O12 N2 T... |

## **5.2** Qualitative analysis

- Quantitative analysis

The quantitative analysis of physical phases is based on the relative intensity of the diffraction lines of each phase.

$$I = I_0 \frac{\lambda^3}{32\pi R}\left(\frac{e^2}{mc^2}\right)\frac{V}{V_0^2} P\left|F_{HKL}\right|^2 \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta} A(\theta) e^{-2M}$$

When measuring with an X-ray diffractometer, above formula can be used for multiphase materials with only slight modifications. Assume that the sample is composed of ***n*** phases, and its total line absorption coefficient is $\mu_l$, then the ***H K L*** diffraction line intensity formula of ***j*** phase is:

$$I_j = I_0 \frac{\lambda^3}{32\pi R^2}\left(\frac{e^2}{mc^2}\right)^2 \frac{1}{2\mu_l}\left[\frac{V}{V_0^2} P\left|F_{HKL}\right|^2 \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta} e^{-2M}\right]_j$$

# **5.2** Qualitative analysis

- Quantitative analysis

$$I_j = I_0 \frac{\lambda^3}{32\pi R^2}\left(\frac{e^2}{mc^2}\right)^2 \frac{1}{2\mu_l}\left[\frac{V}{V_0^2} P\left|F_{HKL}\right|^2 \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta} e^{-2M}\right]_j$$

Since the $\mu_{lj}$ of each phase is different, when the content of phase ***j*** changes, the total $\mu_l$ will change accordingly. If the volume fraction of ***j*** phase is $f_j$ and the irradiated volume ***V*** of the sample is the unit volume, then the irradiated volume of ***j*** phase $V_j = Vf_j = f_j$. In formula, except $f_j$ and $\mu_l$ change with ***j*** phase content, the rest are constants, and their products are represented by $C_j$, then the intensity $I_j$ can be expressed as

$$I_j = C_j f_j / \mu_l$$

## **5.2** Qualitative analysis

- Quantitative analysis

1. Single-line method

By measuring the intensity of a certain diffraction line of the ***j*** phase in the sample and comparing it with the intensity of the same diffraction line of pure ***j***, the relative content of the ***j*** phase in the sample can be determined. This is the single line method, also called the external standard method or the direct comparison method.

If the line absorption coefficient and density of the n-phase contained in the sample are same, then according to formula $I_j = C_j f_j / \mu_l$ . It is obtained that the diffraction line intensity of phase ***j*** is proportional to its mass fraction $w_j$, that is

$$I_j = C\, w_j$$

where ***C*** is the new proportional coefficient. If the sample is pure j phase, then $w_j$ = 100% =1, and $(I_j)_0$ represents the intensity of a certain diffraction line of pure j phase, so we can get

$$\frac{I_j}{(I_j)_0} = \frac{Cw_j}{C} = w_j$$

## 5.2 Qualitative analysis

$$\frac{I_j}{(I_j)_0} = \frac{Cw_j}{C} = w_j$$

- Quantitative analysis

1. Single-line method

The ratio of the intensity of a certain diffraction line of the ***j*** phase in the mixed sample to that of the pure ***j*** phase is equal to the mass fraction of the ***j*** phase.

During quantitative analysis:

- Pure samples and tested samples should be measured under the same experimental conditions.
- Choose the strongest line (highest intensity).
- Use step scanning to obtain the entire diffraction peak, and measure the integrated intensity after subtracting the background.

The single line method is relatively simple, but slightly less accurate, and can only be used for mixtures with the same absorption coefficient of each phase.

$$I_j = C_j f_j / \mu_l$$

$$\downarrow$$

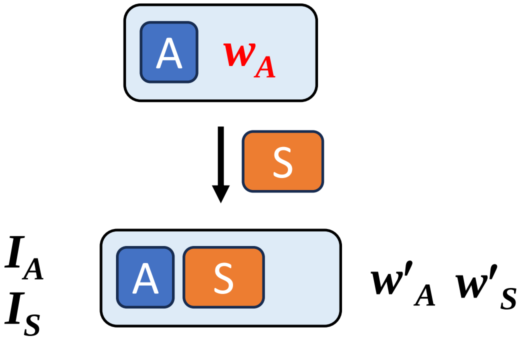
$$I_j = C\, w_j$$

# **5.2** Qualitative analysis

- Quantitative analysis

2. Internal standard method

$$I_j = C_j f_j / \mu_l$$



The internal standard method requires the standard substance **S** to be mixed into the sample to be measured to form a composite sample. According to the formula above, and considering the density of the phase **A** to be measured and the standard material **S**, the relationship between the diffraction line intensity and the mass fraction can be obtained.

$$I_A = C_A \frac{w'_A}{\rho_A \mu_l}$$

$$I_S = C_S \frac{w'_S}{\rho_S \mu_l}$$

$w'_A$ and $w'_S$ are the mass fractions of phase **A** and phase **S** in the mixed sample respectively; $\rho_A$ and $\rho_S$ are the densities of phase **A** and phase **S** respectively; $\mu_l$ is the line absorption coefficient of the composite sample.

# **5.2** Qualitative analysis

- Quantitative analysis

2. Internal standard method

$$\frac{I_A = C_A \dfrac{w'_A}{\rho_A \mu_l}}{I_S = C_S \dfrac{w'_S}{\rho_S \mu_l}}$$

$$\frac{I_A}{I_S} = \frac{C_A}{C_S}\frac{\rho_S}{\rho_A}\frac{w'_A}{w'_S}$$

$w'_A$ and $w'_S$ are the mass fractions of phase **A** and phase **S** in the mixed sample.

If the mass fraction of phase **A** in the original sample is $w_A$, and $w_S$ is the mass fraction of phase **S** in the original sample, then their relationship with $w'_A$ and $w'_S$ is

$$w'_A = w_A(1 - w'_S), \quad w'_S = w_S(1 - w'_S) \xrightarrow{\text{Plug in}} \frac{I_A}{I_S} = \frac{C_A}{C_S}\frac{\rho_S}{\rho_A}\frac{w'_A}{w'_S}$$

$$\frac{I_A}{I_S} = K w_A$$

The above equation is the basic equation of the internal standard method. $I_A / I_S$ has a linear relationship with $w_A$, and $K$ is the slope of the straight line.

## **5.2** Qualitative analysis

- Quantitative analysis

2. Internal standard method

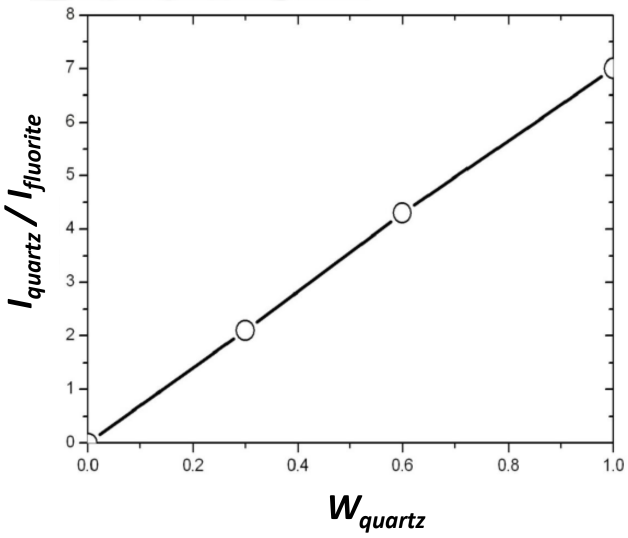
$$\frac{I_A}{I_S} = Kw_A$$

$$K = \frac{C_A}{C_S}\frac{\rho_S}{\rho_A}\frac{1}{w_S}$$

It is usually measured experimentally. For this purpose, a series of samples are prepared, the diffraction intensity is measured and a calibration curve is drawn, that is, the $\boldsymbol{I_A/I_S} - \boldsymbol{w_A}$ straight line, whose slope is ***K***.

When applying, use X-ray diffraction experiments to measure $\boldsymbol{I_A}$ and $\boldsymbol{I_S}$. According to the known slope ***K***, $\boldsymbol{w_A}$ can be calculated from formula above; or calculate the $\boldsymbol{I_A / I_S}$ value and check the calibration curve to directly determine the **A** in the sample to be tested. Phase mass fraction $\boldsymbol{w_A}$.

The internal standard method is the most general and basic method and is suitable for multiphase materials with different mass absorption coefficients. However, the process is cumbersome and a calibration curve must be drawn in advance.



## **5.2** Qualitative analysis

- Quantitative analysis

3. ***K*** value method and reference intensity method

- The internal standard method is a traditional quantitative analysis method, but it has major shortcomings: drawing a calibration curve requires the preparation of multiple composite samples, which requires a large workload; some pure samples are difficult to extract; the number of standards added to the sample is required to be constant……
- In order to overcome the above limitations, many simplified methods have appeared. The more commonly used one is the ***K*** value method. The ***K*** value method is derived from the internal standard method. It only needs to slightly change the formula to get

Internal Standard method

$$\boxed{\frac{I_A}{I_S} = Kw_A \quad K = \frac{C_A}{C_S}\frac{\rho_S}{\rho_A}\frac{1}{w_S}} \longrightarrow \boxed{\frac{I_A}{I_S} = K_S^A \frac{w_A}{w_S} \quad K_S^A = \frac{C_A}{C_S}\frac{\rho_S}{\rho_A}}$$

***K*** value method

## **5.2** Qualitative analysis

- Quantitative analysis

$$K = \frac{C_A}{C_S}\frac{\rho_S}{\rho_A}\frac{1}{w_S} \qquad K_S^A = \frac{C_A}{C_S}\frac{\rho_S}{\rho_A}$$

3. ***K*** value method and reference intensity method

The ***K*** value of the internal standard method includes $W_S$. When the amount of standard phase added changes, the ***K*** value will change accordingly; while the value $K_S^A$ of the ***K*** value method has nothing to do with the amount of standard phase added.

$K_S^A$ can be calculated, but is usually obtained experimentally. For example, if a mixture of same amounts of phase ***A*** and phase ***S*** is prepared, since $w_A / w_S = 1$, so $K_S^A = I_A / I_S$

When applying, add a known amount of **S** phase, measure $I_A$ and $I_S$ from the composite sample, and use the known values to calculate $w_A$.

$$\boxed{\frac{I_A}{I_S} = K_S^A \frac{w_A}{w_S} \qquad K_S^A = \frac{C_A}{C_S}\frac{\rho_S}{\rho_A}}$$

***K*** value method

# **5.2** Qualitative analysis

- Quantitative analysis

3. ***K*** value method and reference intensity method

Advantages:

- The ***K*** value method has nothing to do with the content of the phase to be measured and the internal standard substance.
- As long as a mixed sample composed of the phase to be measured and the internal standard substance is prepared, the ***K*** value can be determined, so there is no need to draw a calibration curve.
- The ***K*** value has a constant meaning. As long as the phase to be measured, the internal standard substance, and the experimental conditions are the same, an accurately measured K value can be used regardless of how the content of the phase to be measured changes.

# **5.2** Qualitative analysis

- Quantitative analysis

## 3. *K* value method and reference intensity method

By further simplifying the K value method, the reference intensity method can be obtained. This method uses corundum ($\alpha$-$Al_2O_3$) as the reference material, and the reference intensity ***K*** values ($I/I_C$) of many commonly used phases have been recorded on powder diffraction cards or indexes. The ***K*** value of substance **A** ($K_S^A$) is equal to the intensity ratio of the strongest lines of the two phases of the substance and a mixture of equal amounts of $\alpha$-$Al_2O_3$.

When there are only two phases in the sample to be tested, because the following relationship exists:

$$w_1 + w_2 = 1 \text{ and } I_1 / I_2 = K_2^1 w_1 / w_2$$

Thus $$w_1 = \frac{1}{1 + K_2^1 I_2 / I_1}$$

By experimentally measuring the $I_1/I_2$ of the two-phase sample, and then borrowing the reference intensity K value ($I/I_C$) on the card, the contents $w_1$ and $w_2$ of the two phases can be calculated.

## **5.3** Determination of lattice parameters

The X-ray diffraction is used to determine the lattice parameters of polycrystalline materials by measuring the glancing angle (θ) of a certain crystal plane and then calculating it using the formula. For cubic crystals there are:

$$a = \frac{\lambda\sqrt{H^2 + K^2 + L^2}}{2\sin\theta}$$

Many problems in research fields such as materials and chemical engineering require the determination of lattice parameters, such as determination of solid solution type, determination of solid phase solubility, determination of macroscopic stress, analysis of chemical heat treatment layers, research on the decomposition process of supersaturated solid solutions, etc.

In the above studies, the changes in lattice parameters are usually very small (on the order of about $10^{-5}$nm). Therefore, it is very important to improve the accuracy of lattice parameter measurement.

# **5.3** Determination of lattice parameters

$$a = \frac{\lambda\sqrt{H^2+K^2+L^2}}{2\sin\theta}$$

- Source of error

X-ray wavelength λ, after accurate measurement, the significant figure can reach seven, and there is no error for general measurement; and the interference surface index ***H K L*** is an integer, and there is no error. Therefore, the accuracy of the lattice parameter a mainly depends on the accuracy of sinθ.

The accuracy of angle measurement (θ) is related to the instrument and method.

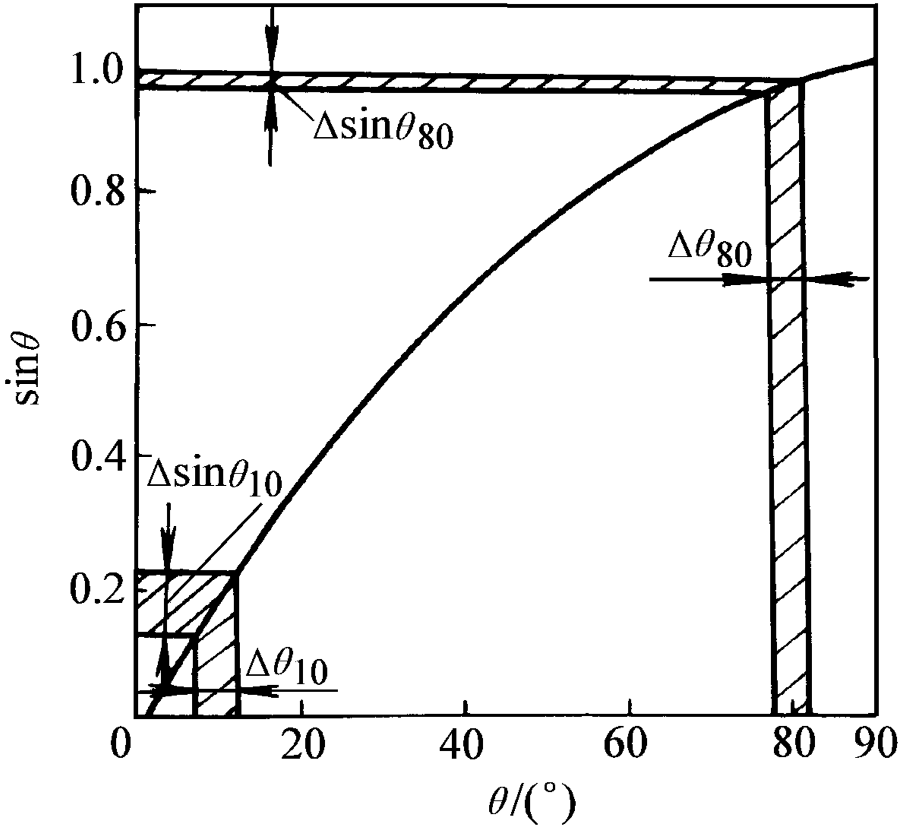
- With the X-ray diffractometer method, the error $\Delta 2\theta$ is about 0.02°. In addition to the error related to the accuracy of 2θ angle measurement, there are also complex errors such as parameter selection and instrument adjustment.

- The accuracy of photographic measurement is low (such as 0.1°), and the main sources of error include the radius error of the camera, the expansion and contraction error of the film, the eccentricity error of the sample, the absorption error of the sample, etc.

# **5.3** Determination of lattice parameters

- Source of error

The change of sinθ with θ is shown in Figure. When θ is close to 90°, sinθ changes most slowly. If the measurement accuracy of θ angle is certain, the sinθ obtained at high θ angle should be more accurate.



Differentiate Bragg's formula to get

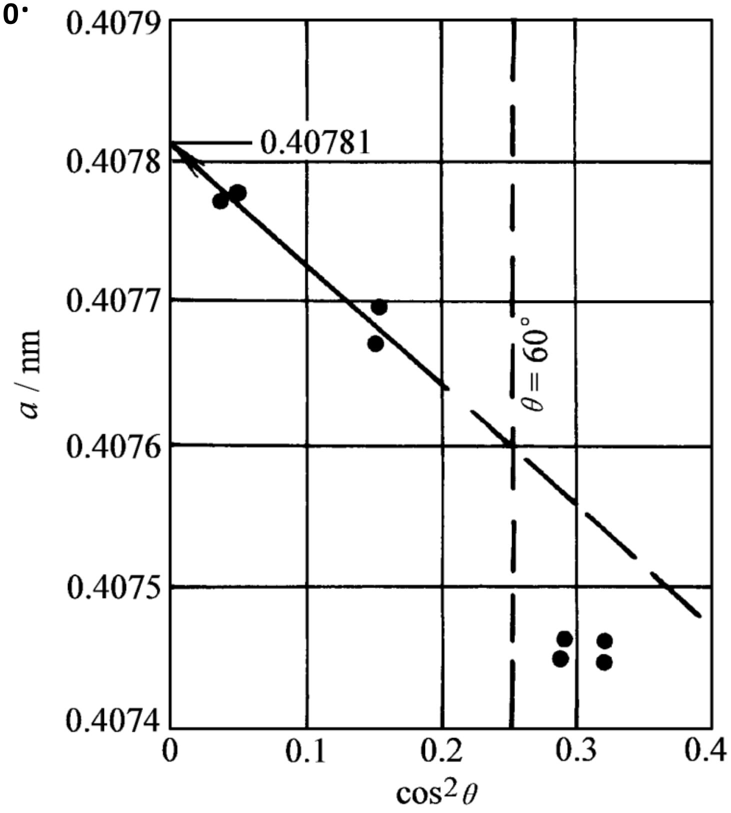
$$\Delta d/d = -\Delta\theta\cot\theta$$

When $\Delta\theta$ is constant, the error will be reduced by using high θ angle diffraction line measurement. When θ approaches 90°, the error will tend to zero. When measuring lattice parameters, you should choose the diffraction line measurement with the highest possible angle.

# **5.3** Determination of lattice parameters

- Graphical Extrapolation

In fact, it is difficult to obtain diffraction lines at the position of θ =90°, but the corresponding **a** value can be calculated based on the θ angles of multiple diffraction lines. Draw **a** straight line with the function of θ as the abscissa and **a** as the ordinate. The straight line is The intersection point of the ordinate ($\theta$=90°) is the exact lattice parameter **$a_0$**.



For the cubic crystal system there are:

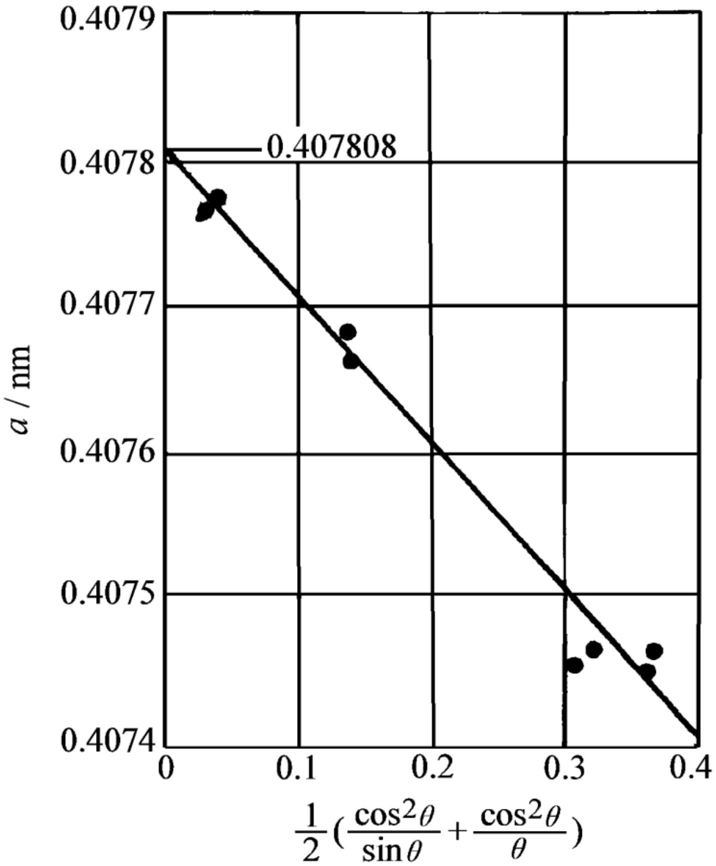
$$\frac{\Delta a}{a} = \frac{\Delta d}{d} = K\cos^2\theta$$

In the above formula, ***K*** is a constant. ***Δa*/*a*** has a linear relationship with **$\cos^2\theta$**. When **$\cos^2\theta$** approaches 0 (θ approaches 90°), ***Δa*/*a*** tends to 0 and ***a*** approaches its true value ***$a_0$***.

# **5.3** Determination of lattice parameters

- Graphical Extrapolation

Extrapolation of $\cos^2\theta$ requires that the $\theta$ of all diffraction lines should be $\theta > 60^{\circ}$, and that the $\theta$ of at least one diffraction line should be above 80°, which is usually difficult to meet.



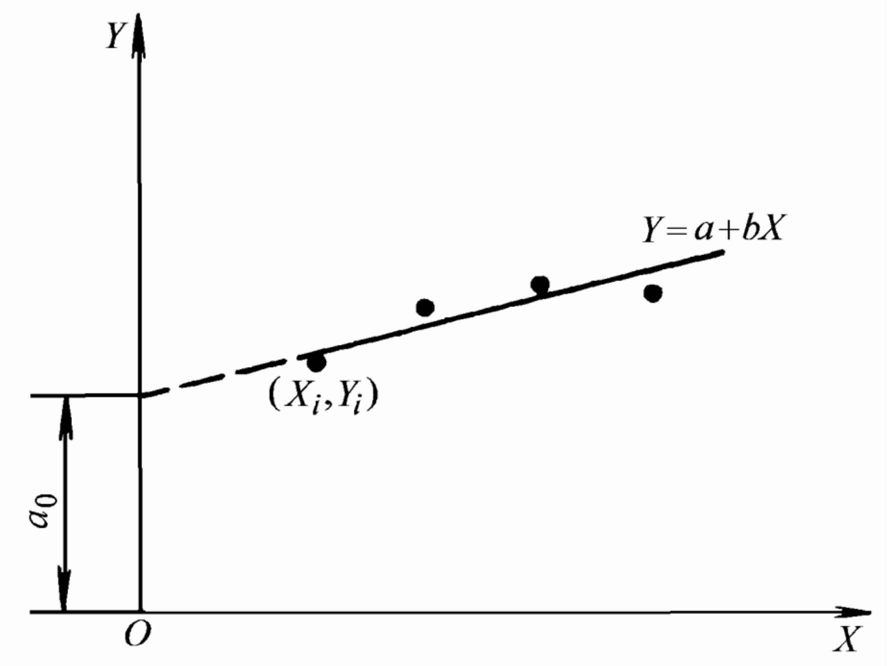
$$f(\theta)=\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$$

It can make $\theta$ in a wider range, f($\theta$) and a have a better linear relationship, see the figure, it is not required that the $\theta$ angle of all diffraction lines is greater than 60°.

# **5.3** Determination of lattice parameters

- Least squares method

Although the straight-line graphical extrapolation method is relatively intuitive, there are still some problems. There are subjective factors in drawing the most reasonable straight line to represent the changing trend of each test point; the scale of the chart is not accurate and it is difficult to meet higher precision requirements.



Using the least squares method for error processing can solve the above shortcomings. In Figure, the ordinate Y is the lattice parameter value; the abscissa X is the extrapolation function value (θ, f(θ)); the experimental point is represented by ($\mathbf{X_i}$, $\mathbf{Y_i}$);

$$Y = a + bX$$

where a is the line intercept and b is the slope.

## **5.3** Determination of lattice parameters

- Least squares method

According to the principle of least squares, the straight line with the smallest sum of square errors is the best straight line. The condition for its minimum error value is:

$$\sum Y = \sum a + b \sum X$$

$$\sum XY = a \sum X + b \sum X^2$$

Solve the system of equations, and the solution ***a*** is the exact lattice parameter value $\boldsymbol{a_{0}}$.

# **5.3** Determination of lattice parameters

- Least squares method

Calculate the exact values of aluminum lattice parameters using the least squares method.

| ***HKL*** | **Irradiation** | **$\theta$/(°)** | **$a$ /nm** | $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ |
|---|---|---|---|---|
| **331** | $K_{\alpha 1}$ | **55.486** | **0.407463** | **0.36057** |
| | $K_{\alpha 2}$ | **55.695** | **0.407459** | **0.35565** |
| **420** | $K_{\alpha 1}$ | **57.714** | **0.407463** | **0.31307** |
| | $K_{\alpha 2}$ | **57.942** | **0.407458** | **0.30550** |
| **422** | $K_{\alpha 1}$ | **67.763** | **0.407663** | **0.13791** |
| | $K_{\alpha 2}$ | **68.102** | **0.407686** | **0.13340** |
| **333, 511** | $K_{\alpha 1}$ | **78.963** | **0.407776** | **0.03197** |
| | $K_{\alpha 2}$ | **79.721** | **0.407776** | **0.02762** |

$\lambda_{K\alpha 1} = 0.154050$ nm, $\lambda_{K\alpha 2} = 0.154434$ nm

## **5.3** Determination of lattice parameters

- Least squares method

Taking the $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ value as **X** and the ***a*** value as **Y**, and substituting the data in Table into the system of equations (page 36), we can get the following equations:

$$\mathbf{3.260744 = 8\mathit{a} + 1.66299\mathit{b}}$$
$$\mathbf{0.67768 = 1.66299\mathit{a} + 0.48476\mathit{b}}$$

The solution of the equation is **a** = 0.407808 nm, which is the exact value of the lattice parameter **a$_0$**.

# **5.3** Determination of lattice parameters

- Least squares method

1. **a** obtained by the least squares method is the Y value when X = 0 ($\theta = 90°$). The error has been eliminated by extrapolation, and the straight line processed by the least squares method has eliminated the accidental error, so a is the accurate lattice parameter value $\mathbf{a_0}$.

2. The graphical extrapolation method and the least squares method are only data processing methods to eliminate errors. The accurate measurement of lattice parameters must be based on accurate measurement data (θ).

3. When using a diffractometer to measure the position of the diffract line (2θ), the customary peak method can no longer meet the requirements. A more reliable method is the three-point parabola method; if higher accuracy is required, the five-point or multi-point parabola method can be used for measurement.

## **5.3** Determination of lattice parameters

- Standard sample calibration method

The standard sample calibration method is also a common method to eliminate errors. For example, Ag powder with a purity of 99.999% (a=0.408613nm) or Si powder with a purity of 99.9% (a=0.543075nm) are used as standard materials, and their lattice parameters are used as standard data.

Mix the standard material into the powder of the sample to be tested, or cover the surface of the block to be tested with a thin layer of standard powder. Calculate the theoretical θ value of a certain diffraction line based on the a value of the standard material, and use the difference between it and the experimental measurement value to treat Calibrate the test sample to obtain more accurate lattice parameters.

The standard sample calibration method is relatively simple in experiment and calculation, but the diffraction lines of the standard sample and the sample to be tested must be very close to each other so that the errors can have the same impact.

# **5.4** X-ray diffraction analysis of amorphous materials and their crystallization process

- Characteristics of amorphous material structure

1. Amorphous materials are short-range order and long-range disorder. It is similar to the crystalline state only in the nearest neighbor relationship, and the second neighbor relationship is obviously different from the crystalline state.
2. Amorphous substances do not have structural periodicity, and there are no concepts such as lattice and lattice parameters.
3. The density of amorphous substances is generally not much different from that of crystals and liquids of the same composition.
4. Amorphous metals maintain metallic properties, and amorphous semiconductors and insulators also maintain their respective properties.
5. Amorphous materials have uniform and isotropic structures.
6. The amorphous structure is a metastable state and has a tendency to spontaneously transform into the crystalline state.

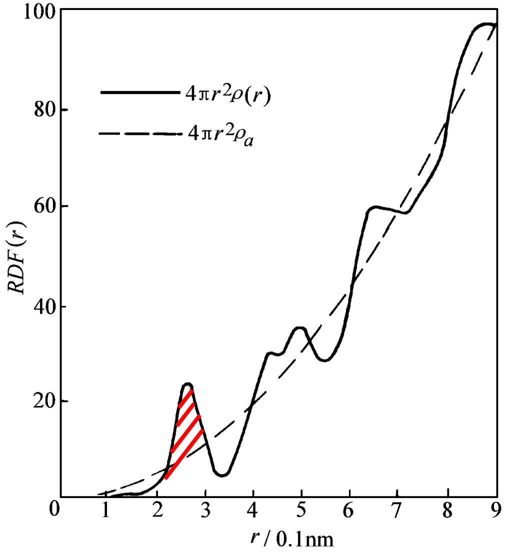
# **5.4** X-ray diffraction analysis of amorphous materials and their crystallization process

- Radial distribution function of amorphous structures

The structure of amorphous materials can be expressed by the radial distribution function (RDF):

$$RDF(r) = 4\pi r^2 \rho(r) = 4\pi r^2 \rho_a + \frac{2r}{\pi}\int_0^\infty S\left[I(s)-1\right]\sin srds$$

The above formula is the radial distribution function of a single atomic substance. The vector $\boldsymbol{r}$ represents the instantaneous position of any atom, $\rho(\boldsymbol{r})$ is the atomic density at a distance $\boldsymbol{r}$ from the origin, $\rho_a$ is the average atomic density of the sample, $\boldsymbol{S}$ is the diffraction vector, and $\boldsymbol{I(s)}$ is the scattering interference function.



The $\boldsymbol{4\pi r^2\rho(r)}$ curve oscillates near the $\boldsymbol{4\pi r^2\rho_a}$ a curve.

The area under each peak of the curve ($\boldsymbol{4\pi r^2\rho(r)}$) is the number of atoms in the corresponding shell, which is called the coordination number. It is an important parameter of the amorphous structure, and the area under the first peak of the curve is called the nearest neighbor coordination number.

## **5.4** X-ray diffraction analysis of amorphous materials and their crystallization process

- Radial distribution function of amorphous structures

Another main parameter of the amorphous structure is the average distance of the atomic shells, which can be obtained from the dimensionless probability density ***g(r)***.

$$g(r)=\frac{\rho(r)}{\rho_a}=1+\frac{1}{2\pi^2 r\rho_a}\int_0^\infty S\left[I(s)-1\right]\sin srds$$

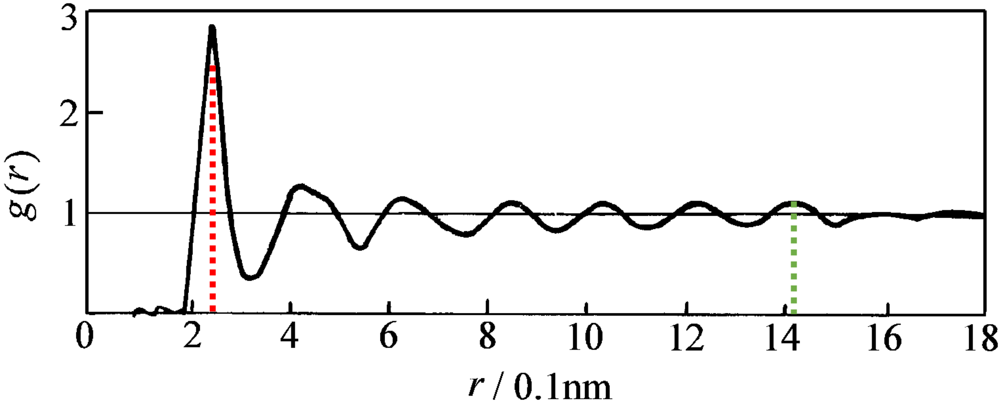


Figure is the two-body probability density function curve of a certain metallic glass. The peak position of the ***g(r)*** curve indicates the position of the maximum value of the atomic distribution probability. The distance from each atomic shell to the central atom can be determined from the peak position on the curve.

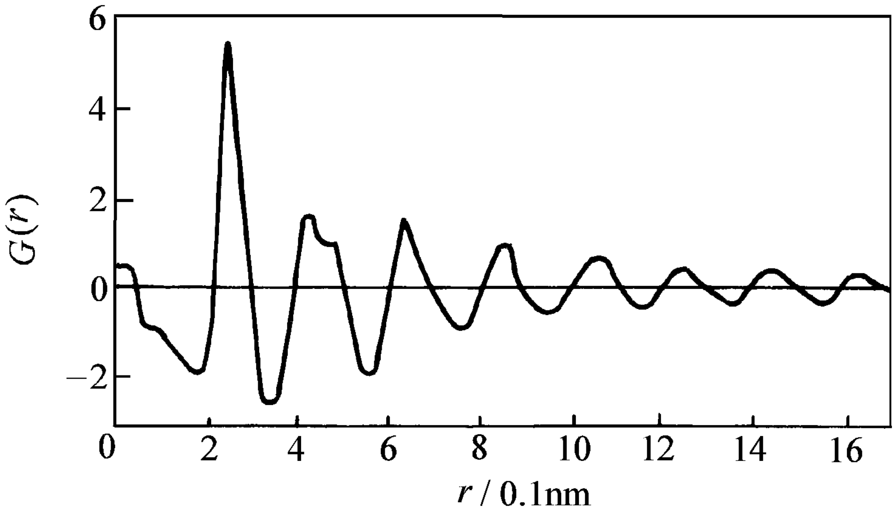
For example, the first peak of the curve is ***$r_1$*** = 0.253 nm, which is approximately the closest distance between atoms, and the short-range order range is about 1.4 nm.

# **5.4** X-ray diffraction analysis of amorphous materials and their crystallization process

- Radial distribution function of amorphous structures

The reduced radial distribution function ***G(r)*** is also commonly used in amorphous structure analysis, namely:

$$G(r) = 4\pi r\left[\rho(r) - \rho_a\right] = \frac{2}{\pi}\int_0^\infty S\left[I(s) - 1\right]\sin srds$$



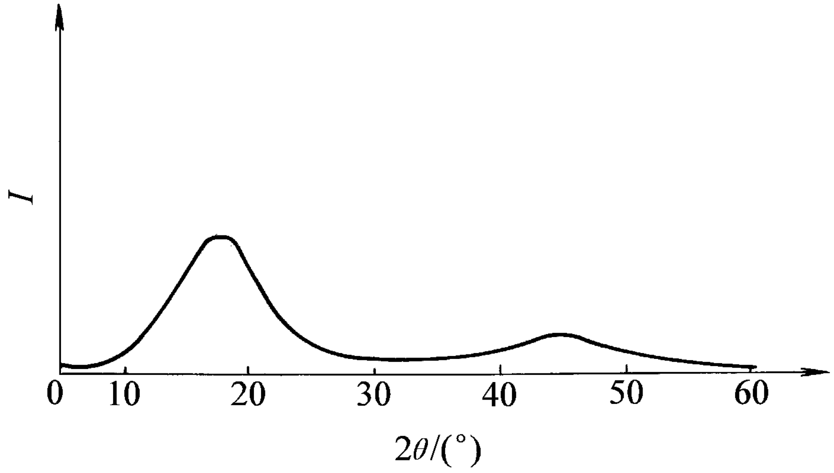
The reduced radial distribution function curve of a certain metallic glass is shown in the figure. It is similar to the two-body probability density function curve. Parameters such as the distance from each atomic shell to the central atom and the short-range order range can also be obtained. From the peak of the distribution function, we can know the atomic position uncertainty caused by static disorder and thermodynamic disorder.

# **5.4** X-ray diffraction analysis of amorphous materials and their crystallization process

- Crystallization Process Analysis

The diffraction pattern of amorphous materials consists of a few diffuse peaks, as shown in the figure, which can provide the following information: the half-height width of the diffuse peak corresponds to the short-range order range $\boldsymbol{r_s}$; the position of the diffuse peak corresponds to the average distance of adjacent molecules or atoms , the approximate value can be given by the quasi-Bragg formula:

$$2d\sin\theta = 1.23\lambda$$



The radial distribution function can give more accurate information about the evolutionary process. For example, as the heating time of amorphous alloys increases, the first peak of the ***g(r)*** curve gradually becomes higher and narrower, the splitting of the second peak gradually disappears, and $\boldsymbol{r_s}$ increases; when it is close to crystallization, the second peak begins to change sharply.

# **5.4** X-ray diffraction analysis of amorphous materials and their crystallization process

- Crystallization Process Analysis

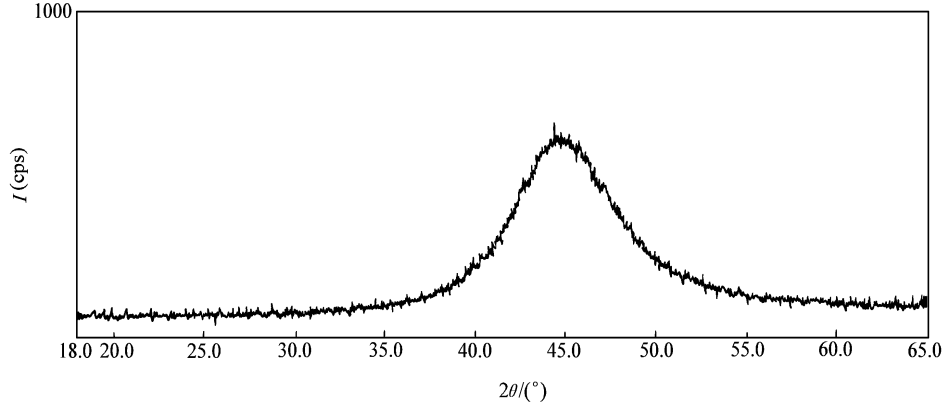


Fig. 1 X-ray diffraction pattern of Ni-P amorphous alloy.

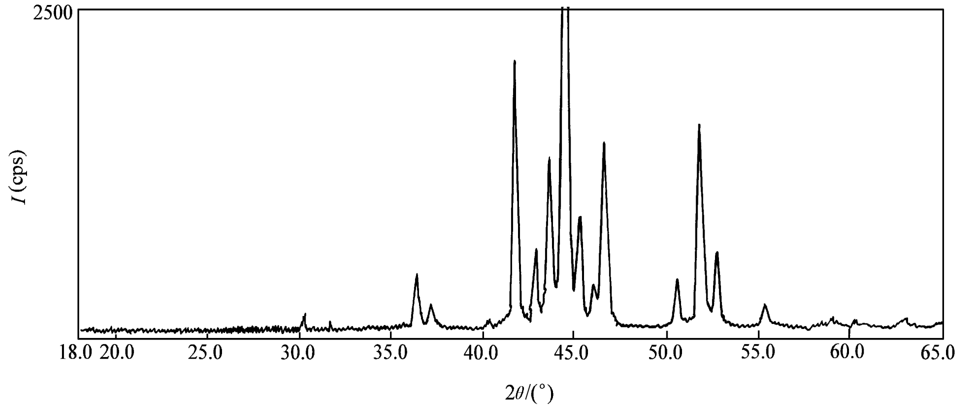


Fig. 2 Diffraction pattern of Ni-P amorphous alloy after annealing at 500℃.

- Comparing Figure 1 and Figure 2, it can be seen that when the Ni-P alloy is amorphous, there is only one diffuse peak in the diffraction pattern.
- when the amorphous alloy is annealed at 500°C, the X-ray diffraction pattern is shown in Figure 2, indicating that the alloy A relatively high degree of crystallization has occurred, and diffraction peaks of Ni and $Ni_3P$ phases have appeared, but a small amount of amorphous phase still exists.

# **5.4** X-ray diffraction analysis of amorphous materials and their crystallization process

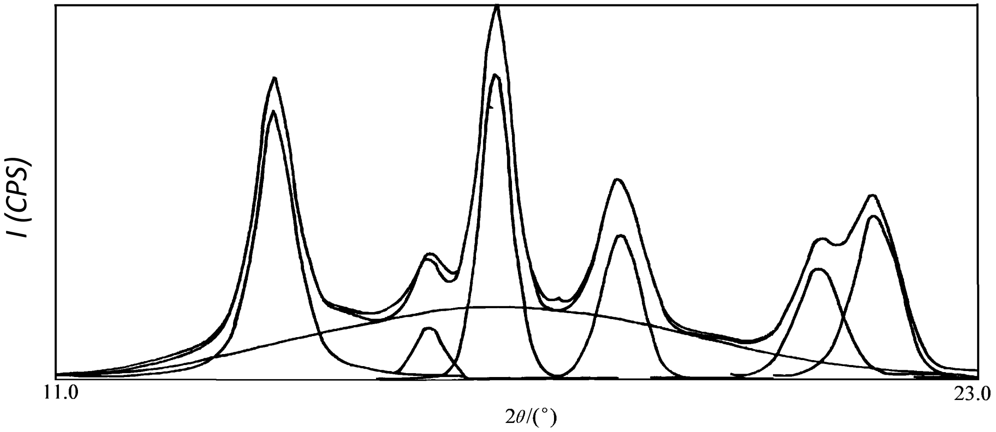
- Determination of crystallinity

The mass fraction of the crystalline phase in the material is expressed by the crystallinity ***Xc***.

$$X_c = \frac{w_c}{w_c + w_a}$$

In the formula, $\boldsymbol{w_c}$ is the mass fraction of the crystalline phase; $\boldsymbol{w_a}$ is the mass fraction of the amorphous phase.

The crystallinity measured by X-ray diffraction method can be calculated by formula:



$$X_c = \frac{I_c}{I_c + KI_c} = \frac{1}{1 + K\dfrac{I_a}{I_c}}$$

In the formula, $\boldsymbol{I_c}$ and $\boldsymbol{I_a}$ are the diffraction intensity of the crystalline phase and amorphous phase respectively, and ***K*** is a constant related to experimental conditions, etc.