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General rules for X-ray polycrystalline diffractometry

多晶体 X 射线衍射方法通则

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General rules for X-ray polycrystalline diffractometry

1 Scope

This standard specifies the analysis method principles, reagents and materials, instruments, samples, analysis steps, result reports, safety precautions, for using polycrystalline X-ray diffractometers, to analyze the phase composition of various polycrystalline materials.

This standard applies to conventional polycrystal X-ray diffractometers. X-ray diffractometers, which are equipped with two-dimensional surface detectors, can refer to this method.

2 Normative references

The following documents are essential for the application of this document. For dated references, only the dated version applies to this document. For undated references, the latest edition (including all amendments) applies to this document.

GB/T 13869-2008 General guide for safety of electric user

GB 18871-2002 Basic standards for protection against ionizing radiation and for the safety of radiation sources

JY/T 009-1996 General rules for X-ray polycrystalline diffractometry

3 Terms and definitions

The terms and definitions, which are defined in JY/T 009-1996, as well as the following terms and definitions, apply to this document.

3.1

X-ray

Electromagnetic waves, which have wavelengths from 10^{-3} nm to 10 nm.

Note: The X-ray wavelength, which is used for crystal diffraction, is 0.05 nm ~ 0.25 nm.

3.2

Crystal

A generalized crystal is a solid, which has a definite diffraction pattern. Its atoms, molecules or ions are arranged in the space a highly ordered manner, according to certain rules, including traditional periodic crystals and non-periodic crystals.

3.3

Polycrystal

A solid powder or bulk object, which is formed by agglomeration of many small grains. It is also known as polycrystalline material.

3.4

Space lattice

In crystallography, the tool used to express the periodic arrangement of structural units in a crystal, which is a collection of periodically repeating points in three-dimensional space.

3.5

Unit cell

The smallest building unit, in which atoms, molecules or ions are regularly arranged, in long-range order, in three-dimensional space. Its shape is a parallelepiped.

3.6

Unit cell parameters

Parameters to describe the parallelepiped unit cell, namely the lengths of the three sides a, b, c, as well as the included angle α (the angle between the b-side and the c-side), β (the angle between the a-side and the c-side), γ (the angle between the a-side and the b-side).

3.7

Lattice distortion

Inhomogeneous strains, that exist inside the lattice.

[JY/T 009-1996, Definition 3.7]

3.8

Crystal system

the horizontal and vertical divergence of the incident rays, the eccentricity of the specimen surface, the absorption of the specimen, the degree of collimation of the instrument, the misalignment of the 1:2 transmission relationship between the θ axis and the 2θ axis, the zero point error, etc. Most of these influencing factors will decrease or disappear, when θ approaches 90°. Therefore, a number of diffraction lines in the high θ range are selected, the corresponding α is obtained according to their θ_{hkl} and hkl, make the α-θ diagram, use the least square method to fit these points AND extrapolate to $\theta = 90°$, where α shall be the smallest error and closest to the true value. The $\cos^2\theta$ is often used to extrapolate the abscissa; other trigonometric functions of θ can also be used, such as $\cos^2\theta/\sin\theta$, $\cos^2\theta/\theta$ or their combinations.

4.4.3 Recommended method

It is recommended to use the full spectrum fitting method, to obtain the unit cell parameters.

Note: The content is quoted from references [19 ~ 24].

4.5 Solving the crystal structure from ab initio polycrystalline diffraction data

For many materials, it is impossible to obtain complete small crystals, that can be used to measure the bulk structure, by the single crystal method. The polycrystalline diffraction spectrum loses the three-dimensional characteristics of single crystal diffraction AND degenerates into a one-dimensional diffraction pattern. The essence of solving the crystal structure from ab initio powder diffraction data, is to restore the one-dimensional diffraction pattern to three-dimensional information; then use the ab initio single crystal method, to solve the structure to obtain the crystal structure.

Note: The content is quoted from references [4, 24 ~ 25].

4.6 High and low temperature diffraction

Some materials often undergo phase change, when the temperature changes, so the high and low temperature diffraction accessories of the diffractometer can be used to dynamically test the change of the specimen diffraction pattern, which is caused by the change of the specimen structure, during the process of heating, cooling or constant temperature, thereby determining the process of phase transition and the result of phase transition, meanwhile determining the phase transition temperature, solid phase reaction temperature, compound decomposition temperature. It can characterize both irreversible and reversible phase transitions.

5 Reagents and materials

5.1 Standard material

The most commonly used is silicon powder; the purity is better than 99.999%; the particle size is between 5 μm and 30 μm; the crystal is perfect; there is no residual stress and too many defects. Silica powder is suitable for the range of 2θ > 29°. When 2θ < 29°, mica is recommended. It is also recommended to use other secondary standard materials. For the principles of selecting standard materials, the names of various standard materials, the PDF card numbers for recording their standard diffraction data, the standard diffraction data of silicon and mica, it may refer to Appendix B.

5.2 Organic solvents

Use organic solvents, such as ethanol and acetone, to clean the utensils.

5.3 Sieves

The mesh size of the sieve, which is used for sieving the sample, is 0.04 mm ~ 0.075 mm.

5.4 Sample preparation tools

Microscope slides, flat glass, agate mortars, clips and other sample preparation supplies.

5.5 Microscope

An optical microscope, which is used to observe the uniform particle size of the sample AND determine whether the specimen plate is flat.

5.6 Specimen plate

Specimen plates without backing, such as hollow aluminum specimen plate, grooved glass specimen plate, single crystal silica, or porous material.

with relevant verification procedures, calibration specifications or calibration methods.

7 Samples

7.1 Pretreatment of samples

The pretreatment of the sample includes grinding, polishing, etc. Equipment for grinding samples includes pulverizers, ball mills, mortars, etc. Different grinding equipment and accessories are selected, according to the hardness of the analyzed specimen AND the influence of impurities that may be introduced.

7.1.1 Grinding

If the sample particles are too large, use an agate mortar and sieve, to make the particles meet the requirements. Grinding often causes decomposition (dehydration) and crystal transformation of the sample. Therefore, the diffractograms shall be compared before and after grinding, to judge the influence of grinding.

7.1.2 Proportion mixing of sample and standard sample

The components shall be pre-dried and ground, to the appropriate particle size, to make the particles meet the requirements. Accurately weigh the sample and standard sample according to the proportioning requirements. Mix the components, so that each component is evenly mixed. There are several mixing methods as follows: quantitatively transfer the powder of each component to be mixed, into a glass vial. Vibrate the vial OR use a shaker to mix, while rotating the vial. Vibrate and rotate it, until the sample is evenly mixed. It may also use an agate mortar, to thoroughly grind and mix the powder. Respectively prepare the specimen into suspensions. Then mix and dry to obtain it, provided that the specimens cannot react with the dispersion liquid. If mixing in a viscous substance (such as Vaseline), the precondition is that the specimen cannot react with viscous substances.

7.1.3 Judging whether the mixture is uniform

Take specimens, which have different mixing times, to perform diffraction scanning. If the obtained spectrum is basically the same, it means that the mixing is uniform. If the diffraction intensity of different phases, on the obtained spectrum, changes greatly, it means that the mixing is not uniform, AND it is necessary to continue mixing.

7.2 Filling of the specimen plate

7.2.1 Usually, use a grooved specimen plate. Evenly fill the specimen in the groove. The surface of the specimen is slightly higher than the surface of the specimen plate. Use a glass slide to press the specimen tightly, so that the surface of the specimen and the surface of the specimen plate are on the same plane.

7.2.2 When there are few specimens, use a non-porous and back-less specimen plate, which is made of single crystal or porous material, to mix the specimen with a volatile solvent, that neither dissolves nor reacts with it. Drop the mixed droplet on the front of the specimen plate. Let it spread. After the solvent evaporates, obtain a thin layer of specimen, on the front of the specimen plate, for measurement.

7.3 Judge whether the specimen plate is available

Quickly scan the specimen plate. If the diffraction line intensity sequence of each substance is similar to that listed in the PDF card, it means that there is no serious preferred orientation, so this specimen plate is available. Otherwise, the specimen plate shall be refilled.

8 Analysis steps

8.1 Startup and parameter setting of the instrument

8.1.1 Power on

Start the instrument, according to the instrument operating procedures.

8.1.2 Setting of instrument parameters

8.1.2.1 Selection of radiation

Radiation of suitable wavelength shall not cause the specimen to produce strong fluorescent radiation AND increase the background of the spectrum. If the number of diffraction lines is large, the interval between diffraction lines is small, AND the overlap is large, THEN, it shall select the radiation of longer wavelength; otherwise, it shall select the radiation of shorter wavelength. The most commonly used radiation is CuK_α radiation.

8.1.2.2 Selection of tube pressure and tube flow

The tube pressure, tube flow, total power used shall not exceed the maximum tube pressure, maximum tube flow, total power, which is allowed by the X-ray tube used. The tube pressure used is generally 3 times ~ 5 times the K excitation voltage of the target material. Unless otherwise specified, the power used usually does not exceed 80% of the full scale.

8.1.2.3 Slit selection

First do a quick scan of 2θ, from about 3° ~ 100°. Determine the scan range, according to the actual position of the peak. The starting angle of the low-angle side scan shall be determined, according to the 2θ position of the first diffraction line.

8.2.2.2 Determine the scan method

Select step scanning or continue scanning, to obtain diffraction patterns.

8.2.3 Data processing

8.2.3.1 Peak searching, calculation of d value and I/I_1

When the computer automatically searches for peaks, it is necessary to select various parameters, for background and noise removal, smoothing, peak searching, to avoid missing peaks or multiple peaks. According to the peak-searching results, the computer gives the diffraction angle 2θ, the interplanar spacing d value, the relative intensity I/I_1 of the diffraction line, the FWHM of the diffraction peak.

8.2.4 Spectrum analysis

8.2.4.1 Retrieving the phase contained in the matching specimen

Use PDF or CCDC index for automatic computer retrieval or manual retrieval, to find out possible diffraction cards or other patterns of known phases. Make careful comparison; finally determine the phase contained in the specimen.

8.2.4.2 Reducing influencing factors

During the analysis, attention shall be paid to the large shift of the d value or the relative intensity data, due to the influence of the solid solution phenomenon, the overlapping peaks of the mixture, the preferred orientation, etc. If there is an obvious preferred orientation, consideration shall be given to re-preparing the specimen OR using a rotating specimen stage, during the measurement, to reduce its influence.

8.2.4.3 Determining that the sample is amorphous or may contain amorphous

If the diffraction pattern of sharper diffraction peaks cannot be obtained, in the diffraction experiment, BUT only a scattering curve with only one or two scattered peaks can be obtained, OR if there is a high background under the crystalline peak, THEN, the sample can be judged as possibly amorphous state or may contain amorphous state.

8.2.4.4 Comprehensive judgment combined with other analysis methods

For the diffraction peaks, whose phase is difficult to determine, in the diffraction spectrum, the elements contained in the compound can be determined by means of the information of the specimen (such as specimen source, chemical composition, processing conditions, etc.) OR by other analytical methods, such as chemical analysis, X-ray fluorescence analysis, electron microscopy analysis, etc., for comprehensive judgment.

8.2.4.5 Analyzing trace phases in the specimen

If the specimen contains trace phase, it is best to obtain the trace phase single-phase sample by extraction and enrichment method; conduct phase analysis on it. If extraction is impossible, it may use the methods, such as increasing the radiation power or extending the data collection time, to make the specimen appear as 3 or more diffraction lines as possible, to carry out the phase analysis.

8.3 Steps for phase quantitative analysis

8.3.1 Preparation before determination

8.3.1.1 Power on and calibration of instrument

Start the instrument according to the provisions of 8.1. Set the parameters. Determine whether the instrument is verified or calibrated, according to the provisions of 6.2.

8.3.1.2 Specimen preparation

Prepare required specimens and standard samples, according to the selected quantitative analysis method. If sample mixing is required, follow the provisions of 7.1.2.

8.3.1.3 Selection of instrument parameter

The selection of instrument parameters shall comply with the provisions of 8.1.2.

8.3.2 Determination

Scan the full spectrum of the specimen. Obtain high-quality reliable data.

8.3.3 Data processing for obtaining phase content

8.3.3.1 Phase analysis

Use Rietveld full spectrum fitting to refine powder diffraction, to carry out data processing, according to the steps specified in the phase quantitative analysis method, to analyze the phase of the diffraction spectrum, thereby determining the phase composition.

8.3.3.2 Modeling

Transfer the diffraction spectrum into the Rietveld full spectrum fitting software. Input the crystal structure model, peak shape model, texture model, background model of the diffraction spectrum, of each constituent phase.

According to the provisions of 8.1.2.

8.6.2 Determination

Carry out test, as specified in 8.3.2.

8.6.3 Data processing

8.6.3.1 Indexing

Collect the diffraction spectrum of the sample. Index the full spectrum. Determine the crystal system, space group, unit cell parameters. Decompose the full spectrum. Restore the one-dimensional diffraction spectrum to a three-dimensional diffraction spectrum. Import the data file into the de-structuring software.

8.6.3.2 Normalization

Observed intensities and normalized structure factors are normalized using Wilson's method.

8.6.3.3 Modeling

The crystal structure model is established, by the Patterson function method, the direct method, the charge inversion method, the maximum entropy method, the genetic algorithm, the simulated annealing method, the model method, etc.

8.6.3.4 Refinement

The crystal structure data, which is obtained by the one-dimensional diffraction spectrum and structural analysis, input into the Rietveld full spectrum fitting software, for refinement.

8.6.3.5 Results

Submit the structural model AND output the results.

8.7 High temperature and low temperature polycrystalline diffraction

If the above various tests need to be carried out, under non-room temperature and variable temperature conditions, it shall use the high temperature or low temperature diffraction accessories.

8.7.1 Preparation before determination

8.7.1.1 Installation of accessories

Install the high temperature or low temperature diffraction accessories on the central

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