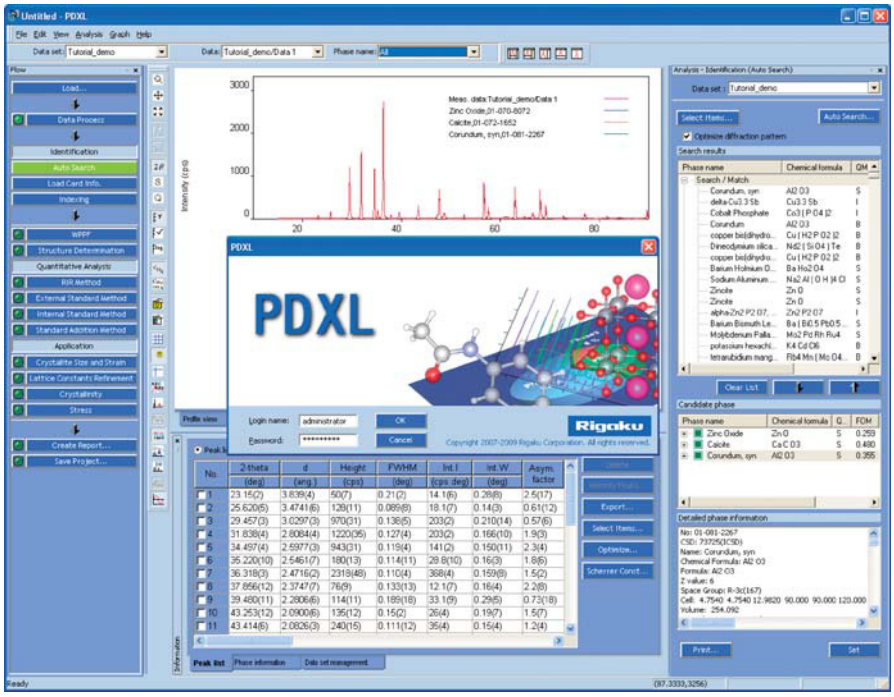
Integrated X-ray powder diffraction software

PDXL

—For more advanced analysis—



1. Introduction

X-ray powder diffraction (XPD) analysis has been widely used in the field of materials science, such as materials development or quality control for over fifty years. However, many scientists and engineers may not be aware of exactly how much information XPD can provide on a sample. Using previous generations of software, high degrees of background knowledge and practical experience have been required to successfully obtain useful analysis results.

In the last five years, both diffractometer and data-analysis software have made significantly advances. New developments of high-speed position sensitive detectors make possible a rapid collection of high-resolution and high-intensity diffraction data. Improvements in PC processing speed make easy the use of an entire experimental pattern, known as "whole-pattern analysis", for a rapid and precise structure analysis of a material. The whole-pattern analysis method is becoming more popular than the conventional analysis methods, which use only certain diffraction peaks to obtain information on specific topics of materials science.

Ab-initio crystal-structure analysis of unknown samples is also gaining popularity in XPD analysis. Many users used to consider this type of XRD analysis difficult because 3-dimensional diffraction data is "flattened" into one- or two-dimensions. There is a misconception that whole-pattern analysis, such as the Rietveld analysis or *ab-initio* crystal structure analysis, is difficult to perform and requires advanced know-how and technical understanding. With this in mind, Rigaku Corporation has developed PDXL, a new application software package created to enable the user who is not familiar with whole pattern analysis to easily perform Rietveld or *ab-initio* crystal-structure analysis with just a few clicks.

Many kinds of information can be obtained from XPD data. PDXL allows the user to perform many types of analysis using a single platform, making it possible to obtain a diverse array of analysis results from one single XPD pattern. The following sections describe how to use PDXL, and several new features in PDXL are also introduced.

2. Analysis

2.1. Automatic peak processing

Most XPD data analysis is performed based on

Fig. 1. Peak list created immediately after loading data.

diffraction-peak information such as peak position, intensity, width, etc. The user used to have to perform several separate data processing steps, including smoothing, background subtraction and peak decomposition, to obtain accurate values for peak position, intensity, and width. PDXL automatically carries out smoothing, background subtraction and peak decomposition, and even creates a peak list as soon as measurement data is loaded (Fig. 1). No user intervention is needed, making PDXL's results free from human error.

2.2. Phase identification

Phase identification is one of the most common objectives of XPD data analysis. Using the PDXL's proprietary Hybrid Search/Match algorithm, crystalline phases (or compounds) presented in a sample can be identified by searching a reference database such as the ICDD's PDF-2.[1] This algorithm checks the degree of coincidence between experimentally measured data and the entries in the reference database, as well as crystallographic data registered in the database with modified lattice constants and preferred orientation within a specified tolerance. Therefore, the Hybrid Search/Match algorithm provides accurate results for the phase identifications of mixtures including solid-solution and highly-oriented samples (see Fig. 2).

The Hybrid Search/Match algorithm consecutively identifies one phase after another in a sample. After identifying the first phase, the peak intensities of the identified phase are subtracted from the experimental pattern. Then the algorithm will look for a second phase in the residual peaks. After the second phase is identified, the peak intensities of the identified phase will again be subtracted from the residual peaks. This procedure will be repeated until no new possible phases can be identified (Figs. 3a–d).

An automatic search for major and minor compounds can be initiated by just clicking the *Execute search*

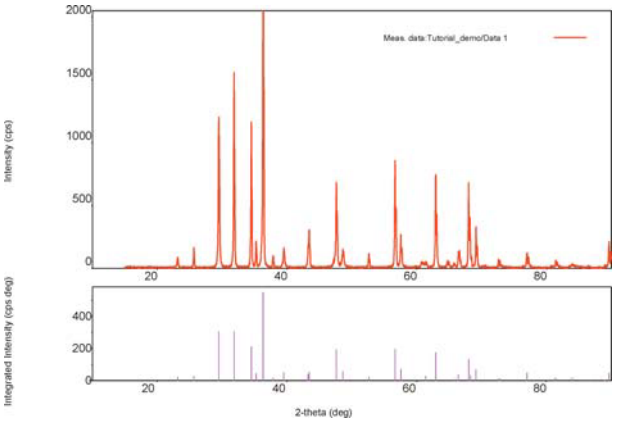


Fig. 3(a). Experimental XRD pattern (top) and integrated intensities (bottom).

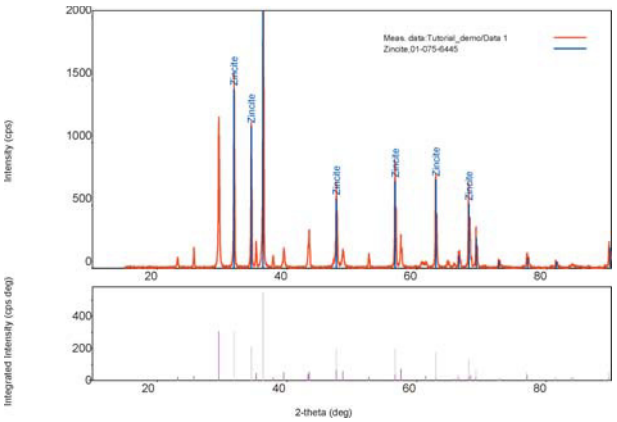


Fig. 3(b). Residual peaks after identifying zincite (see purple bars in the bottom graph).

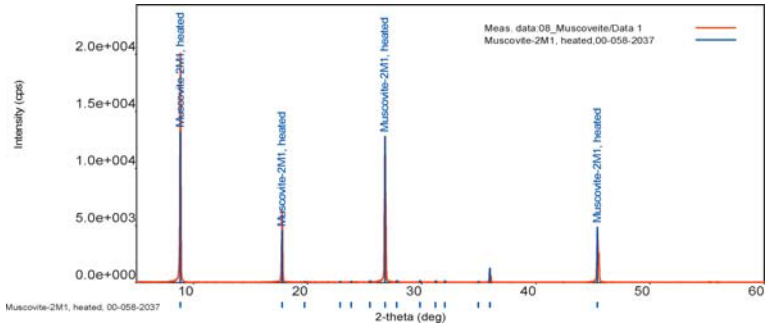


Fig. 2. Identification of a highly-oriented muscovite sample.

[1] See http://www.icdd.com/products/pdf2.htm.

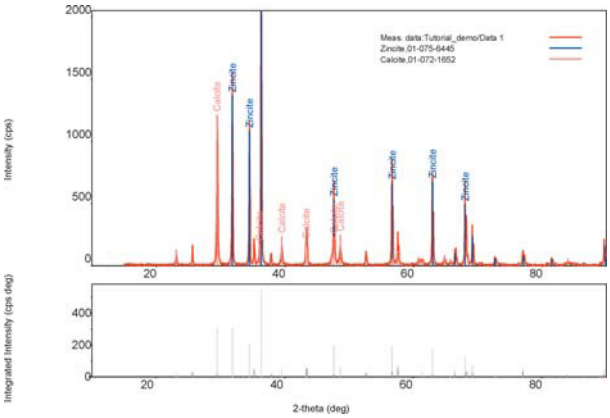


Fig. 3(c). Residual peaks after identifying calcite.

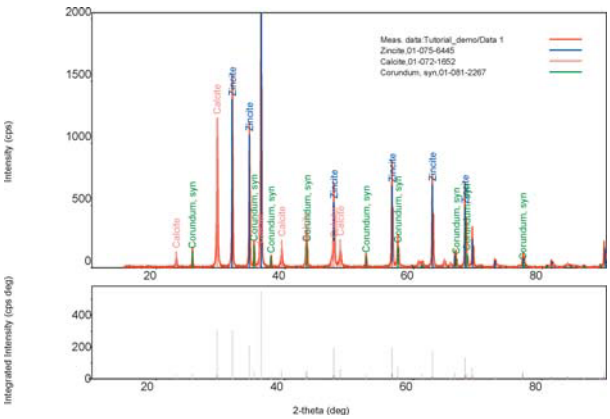


Fig. 3(d). Residual peaks after identifying corundum (most peaks disappear from the bottom graph).

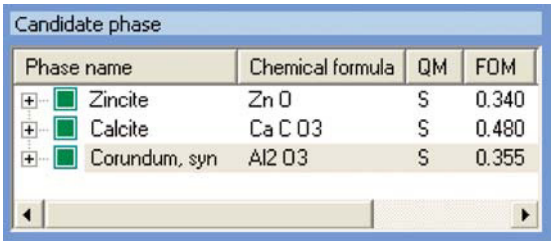


Fig. 4. Determined candidate phases.

button. PDXL will also determine a list of crystalline phase candidates after the search is done (Fig. 4).

2.3. Rietveld analysis

Many consider Rietveld analysis to be a difficult task. PDXL has been designed from the ground up to allow even the novice user to easily perform Rietveld analysis. The application of Rietveld analysis extends beyond crystal-structure refinement; Rietveld analysis also provides the user with accurate lattice constants and quantitative values for the identified phases.

After phase identification, Rietveld analysis requires information on the crystal-structure parameters of each phase. Crystal structure parameters can be obtained in several ways. The easiest method is to obtain the information from the corresponding CIF (crystal information file). If ICSD (Inorganic Crystal Structure Database[2]) has been installed on the user's PC, crystal-structure parameters will be automatically loaded when phase identification is complete. After checking the crystal-structure parameters, click the Refine button to start the Rietveld analysis. Previous analysis packages required a user to input the initial values of the lattice constants, peak-profile parameters, background function, preferred orientation parameters, etc. before starting the refinement. PDXL automatically estimates the initial values of these parameters prior to performing the Rietveld refinement (Fig. 5).

Fig. 5. PDXL main window for Rietveld analysis.

2.4. Analysis-results report

As described above, a lot of information on a sample can be obtained from the analysis of just one XPD pattern. All PDXL results can be viewed in the Analysis Results window (Fig. 6).

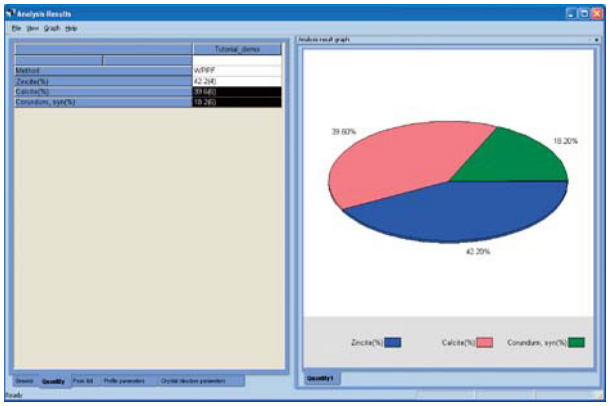


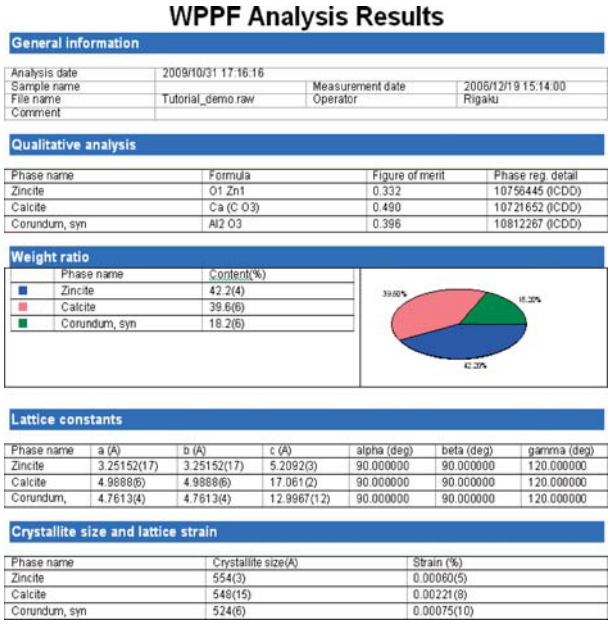
Fig. 6. Analysis Results window.

The user can create graphs of the results, including lattice constants, quantitative XRD analysis, etc. The values obtained from a single analysis can be indicated in a pie chart. PDXL can also generate bar charts to compare results obtained from several XRD patterns.

PDXL makes use of the macro features of Microsoft Word® to create analysis-result reports. PDXL has

[2] See http://www.jaici.or.jp/wcas/wcas_icsd.htm.

several templates for creating reports, which can be used to automatically generate analysis-result reports that are ready for publication (Fig. 7). The template files can also be customized.



WPPF Analysis Results

General information

Analysis date	2009/10/31 17:16:16		
Sample name		Measurement date	2006/12/19 15:14:00
File name	Tutorial_demo.raw	Operator	Rigaku
Comment			

Qualitative analysis

Phase name	Formula	Figure of merit	Phase reg. detail
Zincite	O1 Zn1	0.332	10756445 (ICDD)
Calcite	Ca (C O3)	0.490	10721652 (ICDD)
Corundum, syn	Al2 O3	0.396	10812267 (ICDD)

Weight ratio

Phase name	Content(%)
Zincite	42.2(4)
Calcite	39.6(6)
Corundum, syn	18.2(6)

Lattice constants

Phase name	a (A)	b (A)	c (A)	alpha (deg)	beta (deg)	gamma (deg)
Zincite	3.25152(17)	3.25152(17)	5.2092(3)	90.000000	90.000000	120.000000
Calcite	4.9888(6)	4.9888(6)	17.061(2)	90.000000	90.000000	120.000000
Corundum,	4.7613(4)	4.7613(4)	12.9967(12)	90.000000	90.000000	120.000000

Crystallite size and lattice strain

Phase name	Crystallite size(A)	Strain (%)
Zincite	554(3)	0.00060(5)
Calcite	548(15)	0.00221(8)
Corundum, syn	524(6)	0.00075(10)

Fig. 7. Sample analysis-result report.

2.5. Automation

During the research and development of a new material, it is often necessary to compare the qualitative and quantitative analysis results of related samples synthesized under different conditions. To compare the results of one sample with those of other samples, all experimental datasets need to be analyzed under the same analysis conditions. The automation feature in PDXL makes it easy for the user to do so. Automation applies a predefined analysis process to several different measured datasets, from the initial data processing to report creation. After the setting and saving analysis conditions for one of the measured datasets, the saved conditions can be automatically applied to the analysis of all remaining datasets consecutively (Fig. 8). Therefore, the user only has to select which datasets are to be loaded and analyzed. When the data analysis is complete, all results will be displayed on the screen in an easy-to-compare format (Fig. 9).

Fig. 8. Setting conditions for automation.

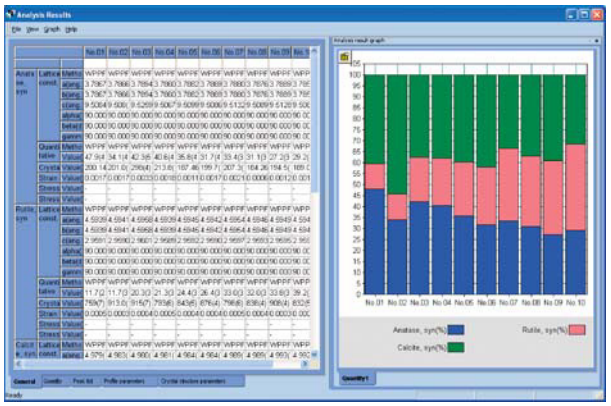


Fig. 9. Comparison of the results of ten samples.

2.6. Quantitative analysis

For quantitative XRD analysis, PDXL uses a well-known conventional "calibration" method, which uses one or more diffraction peaks instead of the entire diffraction pattern. With the calibration method, standard reference samples are used to obtain an accurate quantitative analysis of a sample. Once calibration plots have been created they can be applied to any measured data obtained under the same conditions, as many times as required. PDXL can save the calibration data in the PDXL project format for future use. Similarly, PDXL can save calibration data in the PDXL project format to make corrections to peak positions for lattice constant refinement, peak widths for crystallite size analysis, etc.

3. *Ab-initio* crystal structure analysis

As described above, conventional XPD data is missing certain diffraction-peak information because the three-dimensional XPD data is compressed into one dimension. Therefore, it has traditionally been considered difficult to solve crystal structures using the direct method, which requires a large number of diffraction peaks.

However, the direct space method, which makes use of global optimizations such as the simulated annealing method, has recently been gaining popularity owing to significant improvements in the performance of computers. The direct space method places a molecular-structure model in a unit cell and optimizes the gravity center and Euler angles of the molecule to determine the crystal structure of a compound. The most commonly used method for crystal-structure analysis using XPD data has been to refine the atomic coordinates of another analogous crystal structure by the Rietveld method. On the other hand, the *ab-initio* crystal-structure analysis of a sample with an unknown crystal structure is performed in the same way that a single-crystal structure is determined. Rigaku Corporation has developed a crystal-structure analysis package for PDXL which includes direct method using EXPO2009 [Altomare et

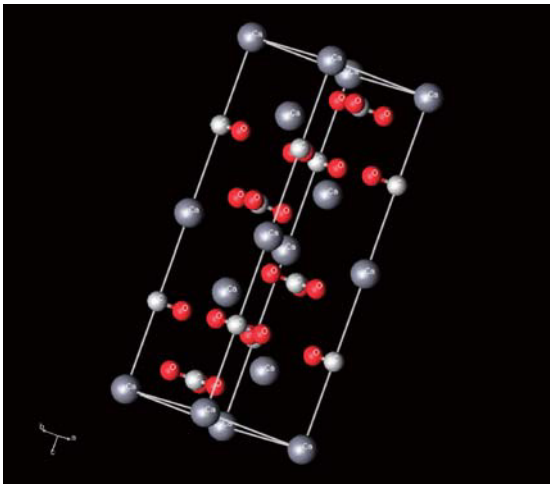


Fig. 10. Crystal structure of calcite, $CaCO_3$.

al., *J. Appl. Cryst.*, **42** (2009), 1197–1202], direct space method and charge flipping method functionality. The structure-analysis package is designed to be easy-to-use, simplifying everything from lattice constant determination by automatic indexing to crystal-structure refinement using the Rietveld method. The crystal structure of a compound determined by PDXL can also be viewed three dimensionally on the user's computer. As an example, the three-dimensional crystal structure of calcite, $CaCO_3$, is plotted in Fig. 10. We believe that PDXL makes crystal-structure analysis more accessible to our users.

4. Conclusions

PDXL has been developed as a comprehensive software package for the analysis of XPD data. The number of scientists and engineers using XPD for materials characterization is growing rapidly, and PDXL makes it possible for those who are not specialists in the field of X-ray diffraction to easily perform Rietveld analysis and *ab-initio* crystal-structure analysis. Many different kinds of information and analysis results can be obtained from XPD data. It is our hope at Rigaku that PDXL will help our users to rapidly obtain useful results, and that these results will be instrumental to advances in a wide variety of scientific fields.