Powder X-ray Diffraction Basic Course Seventh Installment: Lattice constants

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Abstracts

In the seventh lecture of the Powder X-ray Diffraction Basic Course, we will describe “lattice constants.” Lattice constants are a set of fundamental parameters used in various analyses by the X-ray diffraction method. There are three methods for lattice constant calculation; 1. a simple method using the Miller indices of one observed diffraction peak and the *d* value converted from the peak position using Bragg’s law; 2. the least-squares method using multiple diffraction peaks and the Miller indices of each peak; 3. the WPPF (Whole Powder Pattern Fitting) method using a wide range of diffraction patterns. Analysis methods 2 and 3 allow angle calibration using an angle standard reference material. There are external and internal standard methods, each with their own advantages and disadvantages. The WPPF method also allows angle calibration using a peak shift model function without measurement of angle standards. *In-situ* measurements are also possible using a temperature control attachment, where the temperature of the sample can be changed and the diffraction pattern is acquired *in situ*. High-temperature measurements of LSMO (lanthanum strontium manganese oxide), a solid oxide fuel cell, revealed that the behavior of the lattice expansion was different for the a- and c-axes.

1. Introduction

Lattice constants are fundamental parameters of a crystal structure. They are measured, for example, to understand the causes of changes in physical properties. Lattice constants are often evaluated because they are sensitive to changes in ambient conditions such as temperature and pressure. For example, there is a correlation between the lattice parameter change of the cathode materials, LMO ($LiMn_2O_4$) and NMC ($LiNiCoMnO_2$), and battery capacity$^{(1)}$ in the degradation of lithium-ion batteries during repeated use.

The calculation of lattice constants is often performed using the WPPF (Whole Powder Pattern Fitting) method because the acquisition of diffraction patterns is now mostly performed with 1D scan mode$^{(2)}$. Compared to 0D measurement mode$^{(2)}$ with a scintillation counter, the parameters to be considered in the measurement and analysis conditions have also been changed.

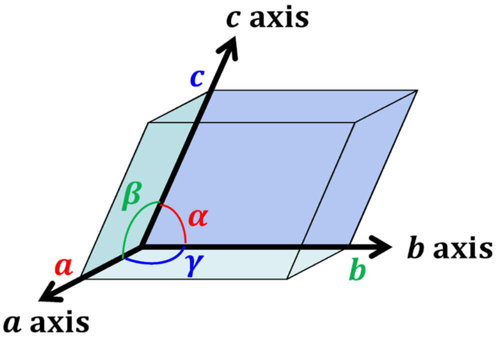

Fig. 1. Lattice constant parameters.

This paper describes the traditional method of calculating lattice constants and the WPPF method, which is currently mainstream. For each method, an overview, advantages and disadvantages, profile functions and parameters to be used, and points of attention are explained. Finally, application examples of lattice constants analysis will be introduced.

2. Lattice Constants

Lattice constants refer to six parameters: the lengths a, b and c of each axis of the unit cell, which is the smallest unit of crystal repetition, and the angles α, β and γ between the axes, as shown in Fig. 1. Note that α is the angle between b and c axes, β is the angle between

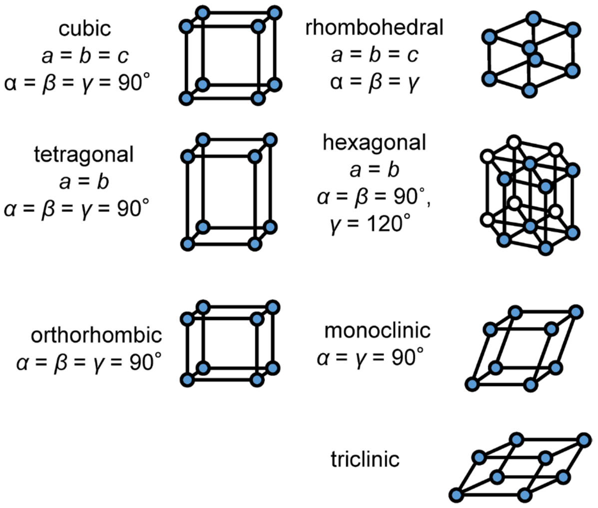

Fig. 2. Constraints on lattice constants parameters in each crystal system.

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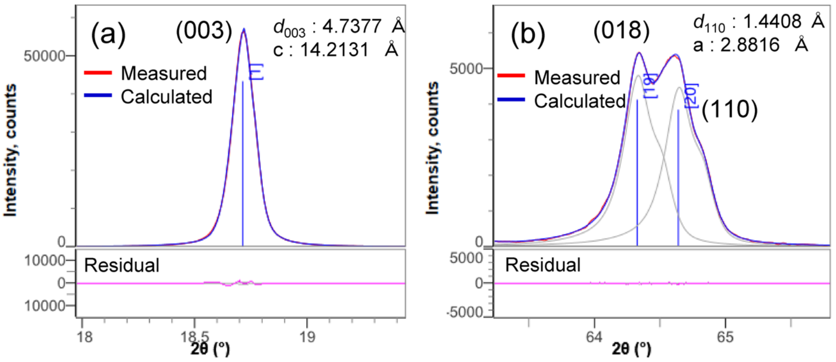


Fig. 3. Diffraction peaks and simplified calculation of lattice constants of $LiNiO_2$ powder. (a): $LiNiO_2$ (003), (b): $LiNiO_2$ (110).

a and c axes, and γ is the angle between a and b axes. As shown in Fig. 2, there are conditions on the length of each axis and the angles between axes depending on the crystal system. A cubic crystal, which has the highest symmetry, has one parameter. A triclinic crystal has the lowest symmetry and has six independent parameters, where the lengths are all allowed to be different and the angles are arbitrary. Metallic monoatomic substances are often cubic or hexagonal, while organic materials are often monoclinic or triclinic.

Bragg's equation "$\lambda=2d\sin\theta$" is differentiated by θ and rearranged to produce this equation:

$$\Delta\delta/\Delta\theta=-d\cdot\cot\theta \qquad (1)$$

Equation (1) indicates that θ should be closer to 90° in order to increase Δd, which is the change in d value, for a slight change in θ. Therefore, diffraction peaks (2θ) at high angles should be analyzed to obtain d-values with high accuracy.

3. Simplified Method for Calculating Lattice Constants

If the Miller index (*hkl*) of each diffraction peak in the XRD pattern can be attributed by qualitative analysis, lattice parameters can be calculated simply from the obtained d value. Figure 3 shows diffraction peaks of (003) and (110) planes of $LiNiO_2$ powder (manufactured by Toshima Seisakusho). The crystal system of $LiNiO_2$ is hexagonal, which means the a- and b-axes of the unit cell are the same length, while the c-axis length is different. The (003) lattice plane is related only to the c-axis. The obtained d_{003} value can be multiplied by 3 to obtain the d_{001} value. Thus, the lattice constant c can be obtained by a simple calculation, although it is done manually. Since the d_{110} value of the (110) plane is the length of d_{110} in Fig. 4, the lattice constant a can be obtained by doubling the value. However, the (110) peak is quite close to the (018) peak. Profile fitting is an effective method to accurately calculate the peak positions in profiles with peaks close together.

In profile fitting, the calculated profile is fitted to the measured profile by the least-squares method so that the residual between the calculated and measured profiles is minimized, as shown in Fig. 3. The peak positions and intensities are then obtained. The full width at half maximum (FWHM) and integrated intensity (corresponding to the peak area) of each peak are also calculated. The calculated profile includes both diffraction peaks and baseline intensities, so there is no need to perform background subtraction. There is also no need to perform $K\alpha_2$ elimination because the 2 : 1 intensity ratio between $K\alpha_1$ and $K\alpha_2$ lines is always taken into account.

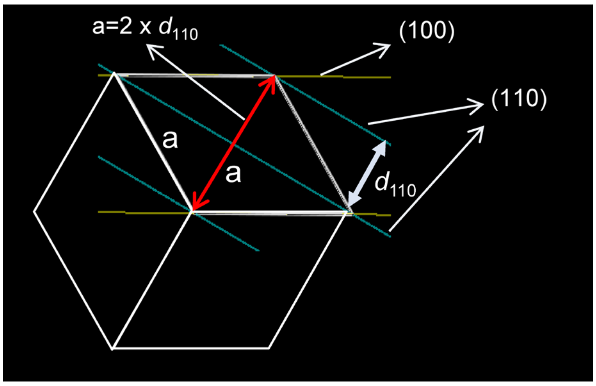


Fig. 4. Schematic diagram of a hexagonal column viewed from above.

The residual at the bottom of Fig. 3 is the intensity obtained by subtracting the calculated intensity from the measured one at each 2θ. The residual is sufficiently small, indicating that the profile fitting is good. However, the lattice constants calculated by this method are larger than those calculated by the WPPF method described below, although they are the same to the second decimal place. This is due to the asymmetrical peak shape caused by an umbrella effect and horizontal divergence effect$^{(3)}$. As a result, because the searched 2θ position is shifted to a lower angle, the calculated d value is large when calculated from Bragg's formula.

4. Method Using the Position of Individual Diffraction Peaks

In this method, the 2θ position of each peak in the diffraction pattern is first determined by peak search. The index of each peak is required for calculating lattice constants. The index (*hkl*) listed on the card identified by qualitative analysis is usually used. As in the previous section, profile fitting is often used as a peak search method. Lattice constants are refined using d values calculated from 2θ values and Miller indices by the least squares method. The number of peaks to be used in the analysis should be several times larger than the number of lattice parameters to be determined.

This method using the positions of individual diffraction peaks was used in the days when only 0D measurements using something like a scintillation counter were available. 0D measurement requires a considerable amount of time; e.g., 10 hours or more, to obtain a wide range diffraction pattern with high resolution and the strongest line reaching 10,000 counts. Therefore, the measurement time was shortened by acquiring only the 2θ range where peaks were observed, while measuring as little of the background range as possible.

Angle calibration can be applied to this method using an angle standard reference material, which cannot be applied to the simple calculation method described in the previous section. Angle calibration is performed by measuring an angle standard reference material with certified lattice constants under the same slit conditions as the test sample, to correct the peak shift to the lower angle side due to the systematic error. The certified value of the lattice constants of the angle standard reference material is taken as the true value. Diffraction angle 2θ is calculated as $2\theta_{hkl}^{calc}$. On the other hand, the actual measured diffraction peak position obtained by profile fitting is defined to be $2\theta_{hkl}^{obs}$. If the systematic error included in the measurement is defined as $\varDelta 2\theta_{hkl}$, then $\varDelta 2\theta_{\mathrm{hkl}}$ is defined as

$$\varDelta 2\theta_{hkl} = 2\theta_{hkl}^{obs} - 2\theta_{hkl}^{calc}$$

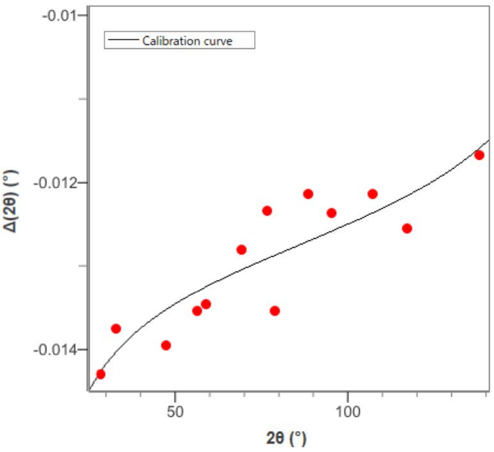


Fig. 5. Angle calibration curve of CeO_2 NIST SRM674a.

The measurement 2θ range of the angle standard reference material should be the same as or wider than the measurement range of the test sample. The method using an angle standard reference material filled on a separate sample plate from the test sample is called the external standard method. On the other hand, the method using an angle standard reference material mixed with the test sample is called the internal standard method. Figure 5 shows the angle calibration curve for NIST 674a CeO_2. SmartLabStudio II uses all peaks identified as CeO_2 in the qualitative analysis to plot the graph. Peaks with low intensity or peaks that are out of the regression curve because they interfere with peaks of the test sample in the case of the internal standard method are excluded from the calculation. $\varDelta 2\theta$ at each 2θ position is calculated from the generated regression curve, and the difference is applied to the profile of the test sample.

The advantages and disadvantages of the external and internal standard methods are summarized in Table 1. In the external standard method, for example, NIST SRM640# is used as an angle standard reference material. If the test sample contains high concentrations of Fe, Co or heavy elements, resulting in high absorption of X-rays by the sample, the penetration depth from the sample surface will differ greatly between SRM640# and the test sample. In such cases, it is necessary to pay attention to elements contained because differences in the penetration depth may cause errors in the angle calibration. If the analysis must be performed using the external standard method, select an angle standard reference material that has an absorption coefficient close to that of the test sample. In the case of the external standard method, more accurate peak positions can be obtained by adjusting the sample height position (half-division adjustment) for each sample plate of the angle standard and the test sample, respectively.

5. Calculation of Lattice constants by the WPPF Method

WPPF stands for Whole Powder Pattern Fitting. A diffraction pattern with relatively wide 2θ range is collected, and a calculated profile is created based on the crystal structure information or the *d–I* pattern of the

Table 1. Advantage and disadvantage of external and internal standard methods

	External standard method	Internal standard method
Advantage	・Can continue to use the filled standard for subsequent measurements. ・Does not require mixing of test and standard samples ・No interference with diffraction peaks of the standard material	・Since the angle standard is mixed with the test sample, the difference in absorption coefficients between the two is cancelled, and any eccentricity in sample height can be corrected.
Disadvantage	・Differences in sample height or absorption coefficient between the standard and test samples will cause errors in angle calibration.	・Requires a mixing operation. ・Costly because expensive angle standard is consumed.

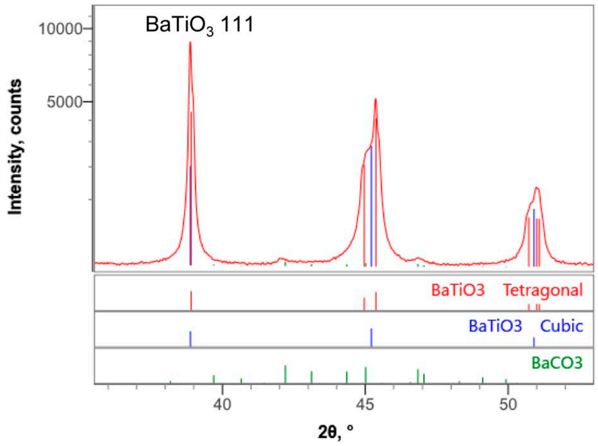


Fig. 6. XRD profile and qualitative analysis results of barium titanate.

card in a database. The split pseudo-Voigt function$^{(4)}$ or FP (Fundamental Parameter) method$^{(5)}$ is usually used as the profile function. Parameters are refined using the least-square method so that the calculated profile matches the measured profile.

Currently, 1D detectors with semiconductor devices are widely used. This allows samples to be measured with high intensity and high angular resolution in about 1/10th of the time compared to 0D detectors. This makes it possible to acquire data in a short time even when measuring from low angle to high angle consecutively, instead of measuring only observed peaks. Since 1D scan mode is standard for current X-ray diffractometers, the WPPF method is the most commonly used method for calculating lattice constants.

Figure 6 shows the diffraction pattern and qualitative analysis results for barium titanate powder (ChemPur). Barium titanate exists mostly as tetragonal with the c-axis slightly longer than the a-axis at room temperature. Except for the 111 reflection, two or three diffraction lines are quite close together. In the case of the split pseudo-Voigt function, parameters related to peak shape in profile fitting include asymmetry factors a_0 and a_1, and η_L and η_H related to the shape of the tail of the peak as well as FWHM. Here, L means the low angle side of the peak and H means the high angle side of the peak. When profile fitting in Section 3 is performed for profiles with diffraction peaks close together as in Fig. 6, the shape of the calculated profile may differ significantly between each index because the asymmetry factors and η factors are refined independently for each individual peak. Therefore, the calculated peak position (2θ) will also contain errors. On the other hand, since parameters related to the profile shape in the WPPF method are determined for each crystalline phase, the peak of each index for the same crystalline phase will have the same shape. Therefore, WPPF method is more suitable for lattice constants calculation in diffraction pattern with peaks close together, such as barium titanate.

Angle calibration is also possible for the WPPF method, and there are two types of correction: angle calibration using the peak shift model function and angle calibration using standard reference materials.

Table 2. Lattice constants of barium titanate powder and standard deviation of c/a

n	a (Å)	c (Å)	c/a
n1	3.99526	4.03506	1.00996
n2	3.99532	4.03500	1.00993
n3	3.99531	4.03503	1.00994
n4	3.99527	4.03496	1.00993
n5	3.99528	4.03505	1.00995
	Standard deviation of c/a (1σ)		0.00001

5.1 Angle calibration using the peak shift model function

The peak shift model function $T(2\theta_i)$ can be expressed by the following equation:

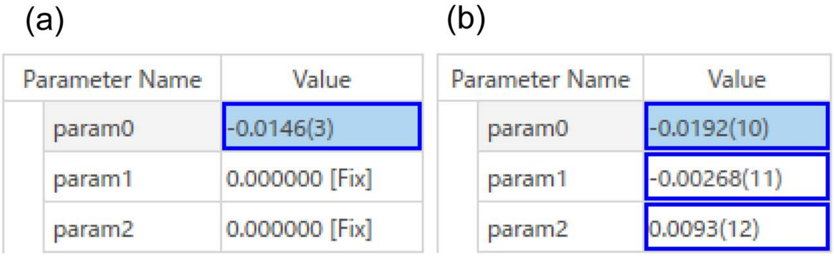
$$T(2\theta_i)=P_0+P_1/\tan 2\theta_i+P_2\cos\theta_i$$

P_0, P_1 and P_2 are parameters to correct for the effects of zero-point error, axial divergence and eccentricity, respectively. Since angle standards are not necessary, there is no need to mix standards or to measure them separately. The process is simple and easy.

The dielectric properties of barium titanate are more closely related to the ratio of c/a than the absolute lengths of the a and c axes. Therefore, if the ratio of lattice constants is to be evaluated, angle calibration is often performed using the peak shift model function, which can be easily performed. Table 2 shows the lattice constants and c/a ratio calculated by the peak shift model function after five repeated measurements of barium titanate powder (Wako Pure Chemical). The standard deviation (1σ) of the c/a ratio was 0.00001, enabling the ratio value to be determined with high precision.

5.2 WPPF method using angle standard reference materials

As described in Section 4, an angle standard reference material with a certified lattice constant such as NIST SRM640# (silicon powder) or NIST SRM674# (CeO_2 powder) is measured in the same 2θ range as the test sample, or over a wider range. The same slit conditions as the test sample should be set when correcting systematic errors. The sampling steps and scan speed can be different for the angle standard reference material and the test sample. Unlike Section 4, in the WPPF method, lattice constants of the angle standard reference material are assumed to be true values. Firstly, the calculated profile is created by fixing lattice constants to the certified values. At this time, the three parameters described in Section 5.1, p_0, p_1 and p_2, are refined to match the measured profile. Then, when fitting the XRD profile of the test sample with WPPF, the determined values of p_0, p_1, and p_2 are fixed and applied to refine lattice parameters of the test sample. Figure 7 shows


(a)

Parameter Name	Value
param0	-0.0146(3)
param1	0.000000 [Fix]
param2	0.000000 [Fix]

(b)

Parameter Name	Value
param0	-0.0192(10)
param1	-0.00268(11)
param2	0.0093(12)

Fig. 7. Peak shift model function. (a) Refinement of only $p_{0,}$ (b) Refinement of p_0, p_1, p_2 against a profile of angle standard material.

the fixing or refinement in parameters of the peak shift model function described in Section 5.1 and this section.

5.3 The use of the split pseudo-Voigt function and FP (Fundamental Parameter) method according to the purpose

When using the WPPF method, the split pseudo-Voigt function or the FP method is often used as the profile function to create a calculated profile. Items evaluated in quality control often include not only the lattice constants, but also the crystallite sizes and the content of each phase. It is also possible to calculate crystallite sizes and lattice strain with the split pseudo-Voigt function, but this requires the measurement of a width standard reference material. The maximum crystallite size that can be analyzed by the split pseudo-Voigt function is up to 100 nm. On the other hand, the FP method allows application of FP profile standards that can analyze crystallite sizes up to 300 nm(6). When quantitative analysis is performed, only one peak from a certain trace crystalline phase is sometimes observed. In such cases, especially when fitting the trace peak with the split pseudo-Voigt function, the fitting may end up with an unrealistic calculated profile shape if the range of the parameters to be refined is not restricted. Based on this, it can be said that the FP method is suitable for the evaluation of crystallite size and quantitative analysis as well as lattice constants.

Fig. 8. Corrosion-resistant infrared heating high temperature attachment Reactor-X.

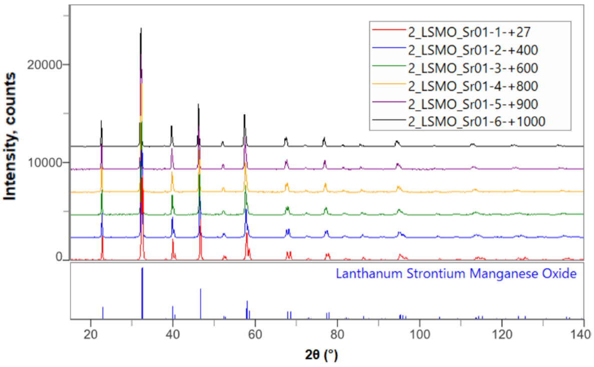


Fig. 9. XRD profile of LSMO at each temperature.

6. Analysis Examples of Lattice Constants

6.1 Lattice constant analysis at each temperature by high temperature measurement

For many materials, the higher the temperature, the more the lattice constants increase due to thermal expansion. By obtaining an XRD profile of a sample at the desired temperature, the lattice constants can be calculated at that temperature. In addition, it is possible to evaluate how the lattice constants change when the temperature changes step by step. This measurement is called "*in-situ* measurement," and is an effective method for observing changes in the crystalline state that occur when the sample environment changes. Figure 8 shows Reactor-X, a corrosion-resistant infrared-heated sample high-temperature attachment. The heat source of this attachment is infrared rays, and the controllable temperature range is from room temperature to 1000°C. Because the heating part and the sample part are separated by quartz glass, this attachment can introduce gases such as hydrogen and oxygen, which cannot be introduced in a normal chamber. The sample plate is made of black quartz glass. Figure 9 shows XRD patterns of LSMO (lanthanum strontium manganese oxide), which is used as an air electrode material in solid oxide fuel cells, at 600 to 1000°C using Reactor-X. The operating temperature of solid oxide fuel cells is normally 600 to 1000°C. Therefore, lattice constants are important parameters for evaluating their operation at high temperatures.

One point to keep in mind for high-temperature measurement is that the sample surface shifts upward as the temperature rises because the sample plate also expands. If the position of the Z-axis, the vertical axis of the sample plane, remains in the room temperature position, even at high temperatures, the sample plane will be eccentric upwards. As a result, in the case of the focusing method, peak positions will shift to a higher angle than the correct peak position. Therefore, when evaluating lattice constants at high temperatures using the focusing method, it is necessary to adjust the height (Z-axis) of the sample at each set temperature. In this study, parallel beam optics with multilayer mirrors and a parallel slit analyzer (PSA) attached to the receiving side were used. When using PSA, the measurement is performed in zero-dimensional mode. 0D measurements take longer time than 1D measurements using focusing method; however, the peak position does not change even if the height of the sample surface changes when a PSA is used. Therefore, the Z-axis does not need to be adjusted at each temperature, making it suitable for precise lattice constant calculation at high temperatures(7).

When performing WPPF on profiles measured with parallel beam optics or profiles where sample height alignment was performed at each temperature in the focusing method, the peak shift model function is refined with LSMO profiles at room temperature. The lattice constants are also refined at this time. For subsequent analysis of profiles at higher temperatures, the lattice parameters should be refined with the determined peak shift parameter values fixed.

Figure 10 shows the change in lattice parameters of LSMO. It can be seen that both the a- and c-axes expand with increasing temperature. The crystal system of LSMO is trigonal, which means that the a- and b-axis are the same length, while the c-axis has a different value. The a- and c-axes change differently, indicating that the expansion is anisotropic.

Multiple profiles were analyzed simultaneously in SmartLab Studio II using a template file for WPPF analysis, and the refined lattice parameters were displayed on the analysis software screen. The results are shown in Figure 10. The horizontal axis can be changed from the sample name to the measured temperature. By using a template file, it is not necessary to select a model card each time, meaning that the analysis can be performed quickly.

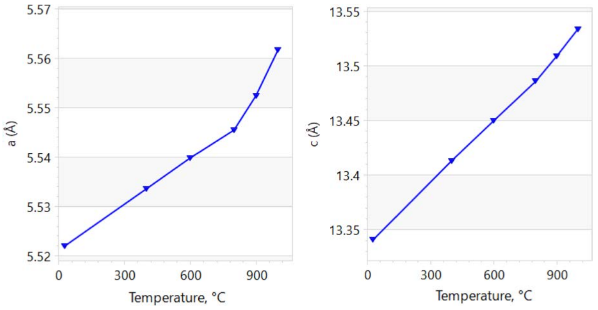


Fig. 10. Temperature dependency in lattice constants of LSMO.

6.2 Evaluation of lattice constants of perovskite structure: Dielectric material $Y(In_x\ Mn_{1-x})O_3$

Perovskite-type oxide ferroelectrics are represented by ABO_3 chemical formula. Physical properties such as phase transition temperature and electrical conductivity vary depending on the type of cations in A and B sites and the ratio of two elements in solid solution at the same site. Figure 11 shows diffraction patterns of $Y(In_x\ Mn_{1-x})O_3$ for ($x=0.2$, 0.4, 0.6, 0.8). In has a larger atomic radius than Mn; therefore, the peak positions shift to the lower angle side when the amount of In increases, indicating that the lattice constants are larger.

When performing WPPF, the method of refining parameters while keeping a constraint on the intensity ratio between diffraction peaks determined based on the crystal structure information of atomic positions and occupancies is called Rietveld analysis(8). On the other hand, the method that matches the calculated profile to the measured intensity of each peak while ignoring the intensity ratio between diffraction peaks is called pattern decomposition(9). If only lattice parameters are

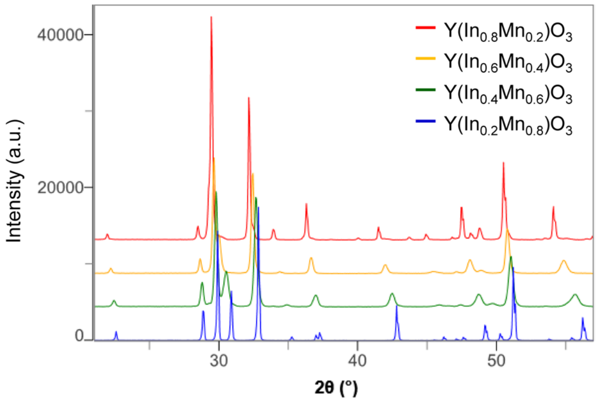


Fig. 11. XRD profiles of Y (In_xMn_{1-x}) O_3.

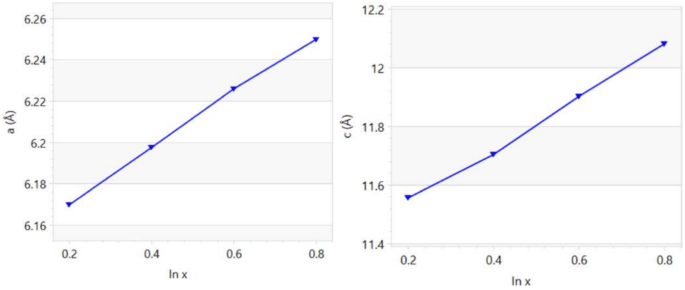


Fig. 12. Change in lattice parameters with change in solid solubility of Y (In_xMn_{1-x}) O_3

to be calculated as evaluation items, these can be obtained using intensity decomposition. In this case, the crystal structure information about atomic positions and occupancies is not always required, and lattice parameters can be refined even with a database such as ICDD PDF-2 that does not contain crystal structure information.

Using a database with crystal structure information such as ICDD PDF-4+, PDF-5+ (PDF-4+ and PDF-4/Organics merged from 2024 edition) and COD, the occupancy of In and Mn at the same site can be determined. Occupancy is the probability of each element being present at a given atomic position. The occupancy value ranges from 0 to 1. Usually, a constraint is applied such that the sum of occupancies of two elements is 1.0. When the value of occupancy is varied, the intensity ratio changes, especially on the low angle side. Note that even if the value of the occupancy is changed, if the values of lattice constants are the same, the peak position of the calculated profile does not change.

Figure 12 shows the changes of lattice parameters for $Y(In_x Mn_{1-x})O_3$ calculated by Rietveld analysis. For both a- and c-axes, these changes can be approximated by a straight line, indicating a proportional relationship between solid solution ratio and lattice parameters. This is called Vegard's law. Even if there is a sample whose solid solution ratio is unknown, the solid solution ratio of In and Mn can be determined from the regression line by calculating the lattice parameters.

7. Summary

We explained how to calculate lattice parameters, advantages and disadvantages of each method, the principle of angle calibration, points to keep in mind when measuring and analyzing, and finally measurement examples. Regarding analysis operations, we highly recommend SmartLab Studio II because of its improved usability, such as batch analysis using a template file and the ability to easily display lattice parameter changes for multiple samples in the software. The accuracy and precision of obtained lattice parameters depend on the presence of eccentricity errors and the intensity and resolution of the diffraction profiles. For details on how to set up measurement conditions to obtain higher quality data, please refer to Part 2(10) and Part 3(11) of this Powder Basic Course.

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