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ANALYSIS OF POWDER DIFFRACTION PATTERNS OF MONOCLINIC CRYSTALS

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SUMMARY

This study describes an analtical way for determination of unit cell parameters from powder diffraction patterns of monoclinic crystals. The determining of unique axis parameter from any monoclinic diffraction pattern is well-known in the existing literature. In the present study, after finding unique axis parameter, a suitable way of solving the other unknown unit cell parameters has been treated in the matrix equation. Many solutions of the other unknown parameters can be obtained by changing of the indices in the given matrix equation. A criter to chose the correct cell parameters from these solutions has been given by indexing of the pattern within any assumed error with each solution. As an application of this analysis way, the diffraction data of $MgWO_4$ taken from literature has been solved.

MONOKLİNİK KRİSTALLERİN TOZ DİFRAKSİYON KALIPLARININ ANALİZİ

ÖZET

Bu çalışma, monoklinik kristallerin toz difraksiyon kalıplarından birim hücre parametrelerinin belirlenmesi için analitik bir yol

tanımlar. Literatürde, herhangi bir monoklinik difraksiyon kalıbından tek eksen parametresinin belirlenmesi iyi bilinmektedir. Şimdiki çalışmada, tek eksen parametresinin bulunmasından sonra, diğer bilinmeyen birim hücre parametrelerinin çözümünün uygun bir yolu matris denklemi içerisinde türetilmiştir. Verilen matris denklemi içinde indislerin değiştirilmesiyle diğer bilinmeyen parametrelerin birçok çözümü elde edilebilir. Herbir çözüm ile kabul edilen herhangi bir hata içinde kalıbın indislenmesiyle bu çözümlerden doğru hüçre parametrelerini seçmek için bir kriter verilmiştir. Bu analiz yolunun bir uygulaması olarak $MgWO_4$'dün literatürden alınmış difraksiyon datası çözülmüştür.

1- INTRODUCTION

Angles or distances measured in the powder diffraction pattern can be expressed as $Q_i(obs)=1/d^2=d^{*2}=4\sin^2\theta/\lambda^2$ in the reciprocal units. This is simpler than the real space equivalent[1]. The problem is fitting these observed $Q_i(obs)$'s with the calculated $Q_i(cal)$'s. This fitting procedure is called indexing of the pattern. Several methods were developed for the indexing of diffraction patterns. These methods may be considered essentialy two groups as graphical and analtical methods.

If the pattern has at least monoclinic symmetry, after the identification of one edge of the conventional unit cell the indexing may be accomplished by the graphical methods and these methods can also be used to index the other higher symmetry patterns [2,3,4,5]. The graphical methods are suitable for long spacing compounds because these are liable to fail in cases with a high proportion of missing reflexions [6]. If the pattern has higher symmetry, the analtical methods [6,7] to index of the pattern are more sistematic and simpler than graphical. But these analtical methods do not explain monoclinic

patterns.

The general method based on the proces of finding out a zone by assuming the specimen of the pattern under examination as triclinic was discovered analticaly [8,9,10,11]. Although this method, the general procedure fails to deduce the solution owing to insufficient or inaccurate data. For such cases there could still be another method of evading the difficulty by assuming the specimen of the pattern as monoclinic from the beginning [11].

For indexing monoclinic patterns, the method based on determining unique axis parameter [11,12] and the other based on solwing simultaneously equations [13] were discovered analticaly. In the present study, a series of procedures based on combining these two methods has been established for indexing of monoclinic patterns. There are four unknown unit cell parameters in the monoclinic case. One of them which is called unique axis parameter can be determined in any set of Q_i(obs)'s. After determining unique axis parameter, a matrix solution has been treated to determine the other three unit cell parameters. A program of these procedures has been prepared for calculations and as an application of this analysis way, the indexing of the diffraction data of $MgWO_4$ taken from literature has been given.

2- ANALYSIS OF MONOCLINIC PATTERNS WITH MATRIX SOLUTION

Let the powder pattern under examination be not triclinic pattern. So the lowest symmetry space of this pattern can be considered as a monoclinic system.

2.1- Determination of unique axis parameter

In the monoclinic system, let the unique axis be S_3, the interplanar spacing is

$$Q(h,k,l)=1/d^2=S_1h^2+S_2k^2+S_3l^2+S_4hk \qquad -1-$$

where $S_1=a^{*2}$, $S_2=b^{*2}$, $S_3=c^{*2}$, $S_4=2a^*b^*\cos\gamma^*$ in the reciprocal space. Shortly, the way of determining S_3 is based on

$$\Delta Q=Q(h,k,l)-Q(h,k,l')=(l^2-l'^2)S_3 \qquad -2-$$

where $(l^2-l'^2)$ are integers such as (1,3,4,5,8,9) for example (1,3,5,9,...) for primitive translation, and (4,8,12,...) for centred translation lattices [11].

In any set of Q_i(obs)'s, there are many pairs of Q_i(obs), Q_j(obs) corresponding to reflections (h,k,l) and (h,k,l') and differences between these pairs satisfy equation 2. It is produced all differences between Q_i(obs)'s as

$$\Delta Q_n=Q_i(\text{obs})-Q_j(\text{obs}). \qquad -3-$$

Because of $S_3=\Delta Q/(l^2-l'^2)$, each of these produced ΔQ_n's is divided with each of these numbers (1,3,4,5,8,9) seperately i.e. $\Delta Q_n/1$, $\Delta Q_n/3$, ... $\Delta Q_n/9$. These values are arranged according to increasing order of magnitude. There are some values, in this arranged form, which are repeated many times in any assumed observational error. The genuine value of them which is repeated by the largest number is chosen as S_3 [11,12].

2.2- Production of possible solutions of other parameters

After determining S_3, q_j's can be produced as $q_j=Q_i(\text{obs})-S_3l^2$ for l=0,1,2,3,4. Some values in q_j appear more than twice in any assumed observational error. These values are most probably Q(h,k,0)'s. Some of these pairs has an Q_i(obs) value. These Q_i(obs)'s have been chosen

as observed Q(h,k,0)'s.

In order to determine the other parameters, the simplest algebraic relation between Q(h,k,0) values is

$$2(Q(h_1,k_1,0)+Q(h_2,k_2,0))=Q(h_3,k_3,0)+Q(h_4,k_4,0) \qquad -4-$$

where $h_3=h_1-h_2$, $k_3=k_1-k_2$; $h_4=h_1+h_2$, $k_4=k_1+k_2$ [9]. It is enough to use three Q(h,k,0) quadratic forms to solve the other three unknown parameters. Obviously, it is possible to take one of that configurations of $Q(h_1,k_1,0)$,$Q(h_2,k_2,0)$,$Q(h_3,k_3,0)$ or $Q(h_1,k_1,0)$, $Q(h_2,k_2,0)$, $Q(h_4,k_4,0)$. For the first configuration, the equation system becomes as follow:

$$\begin{aligned} Q(h_1,k_1,0)&=S_1h_1^2+S_2k_1^2+S_4h_1k_1 \\ Q(h_2,k_2,0)&=S_1h_2^2+S_2k_2^2+S_4h_2k_2 \\ Q(h_3,k_3,0)&=S_1h_3^2+S_2k_3^2+S_4h_3k_3. \end{aligned} \qquad -5-$$

Thus the problem has been changed into three equations with three unknown parameters. Finaly, using the matrix notation the equation above is expressed as

$$Q=AS \qquad -6-$$

where

$$Q=\begin{bmatrix} Q(h_1,k_1,0) \\ Q(h_2,k_2,0) \\ Q(h_3,k_3,0) \end{bmatrix}, \quad A=\begin{bmatrix} h_1^2 & k_1^2 & h_1k_1 \\ h_2^2 & k_2^2 & h_2k_2 \\ h_3^2 & k_3^2 & h_3k_3 \end{bmatrix}, \quad S=\begin{bmatrix} S_1 \\ S_2 \\ S_4 \end{bmatrix}.$$

In the matrix solution rules [14], this matrix equation has been

solved within any assumed cycle of $(h_1,k_1,0)$ and $(h_2,k_2,0)$ indices. In this way, many S_1,S_2,S_4 solution sets are produced.

2.3- Determination of the correct cell parameters

One of S_1,S_2,S_4 solution sets is superior to the others. In fact, condition of finding correct solution set is to try indexing of all $Q_i(obs)$ values with every S_1,S_2,S_4 solution set and S_3 which was determined before. The simplest relation of indexing procedure is

$$error=|Q_i(obs)-Q_i(cal)|< 0.0005 \qquad -7-$$

where $Q_i(cal)=S_1h^2+S_2k^2+S_3l^2+S_4hk$ within any assumed cycle of (h,k,l) indices [13].

The next step to investigate how many of $Q_i(obs)$ values can be indexed for every solution set. The number of indexed lines (hereinafter termed N) denote that the solution set is a superior one or an inferior one. If a set gives maximum number of observed indexed lines i.e. N(max), that solution set is accepted as the correct cell parameters of the pattern under examination.

3- EXAMPLE

The diffraction data of $MgWO_4$ taken from Ishida and Watanabe [11] has been given in table 1. The data is a standart file in National Bureau of Standards Circular(1953) p.85 which is a monoclinic sample carried out by Ishida and Watanabe[11]. This diffraction data has been used to demonstrate the actual procedure mentioned above.

Firstly, from the unique axis analysis, it has been found that $S_3=0.0310$. After that, the q_3 values have been produced and observed Q(h,k,0)'s have been chosen as shown in table 2. There may be many four Q(h,k,0) values satisfying equation 2 in observed Q(h,k,0)

values. But one of them is enough to solve. In this sample these $Q(h,k,0)$'s have been fixed as $Q_1=0.0457$, $Q_2=0.1649$, $Q_3=0.2077$, $Q_4=0.2123$. According to equation 6, there is a real solution of S_1, S_2, S_4 for every possible $(h_1,k_1,0)$ and $(h_2,k_2,0)$ indices. Many S_1,S_2,S_4 solution sets have been produced within the cycle of $(h_1,k_1,0)$ and $(h_2,k_2,0) \leq (2,2,2)$.

After that, every of these solution set with S_3 (=0.0310) has been tried to index all of $Q_i(obs)$ values in equation 7 under the accepted error < 0.0005 where the indices in $Q_i(cal)$ has been taken within the cycle of $(h,k,l) \leq (4,4,4)$. Some more possible solution set has been carried out with the aid of N which was termed the number of indexed lines. These solution sets has been given with N together in table 3. As shown in table 3., the maximum number of observed indexed lines is 23 (i.e. N(max.)=23). So the best suitable unit cell parameters set has been fixed as $S_1=0.0861$, $S_2=0.0457$, $S_3=0.0310$, $S_4=-0.0906$.

Lastly, all of the $Q_i(obs)$ values of the pattern must be satisfied by the chosen parameters. This stuation dependent the accepted error. The pattern can be indexed completely by the changing error. The indices all of $Q_i(obs)$'s of the pattern produced by fixed unit cell parameters with error < 0.0030 has been given in table 4.

4- DISCUSSION

The described way of analysis powder diffraction patterns of monoclinic crystals has been succesfuly applied to determine the unit cell parameters. This analysis way of monoclinic patterns may be preferred to solve if the number of $Q_i(obs)$ lines are large because it may fails when equation 4 does not satisfies.

As shown in table 4., the chosen parameters i.e. $S_1=0.0861$, $S_2=0.0457$, $S_3=0.0310$, $S_4=-0.0906$ index all of observed lines with error=$|Q_i(obs)-Q_i(cal)| < 0.0030$. This is perhaps large error. But all

diffraction patterns have an experimentall error. Limits of these errors depend on the experimental conditions. For determination accurate unit cell from powder pattern, the accuracy of Q_i(obs)'s is great important. So it can be said that the best fixed unit cell parameters produced via the method mentioned above is perhaps approximate values of correct cell because there is always measurement error in Q_i(obs)'s. It was not worked to find refined parameters in this paper because refined lattice parameters of this sample were determined by Ishida & Watanabe [11] as S_1=0.0855, S_2=0.0455, S_3=0.0310, S_4=-0.0900. By comparing these two results, it is seen that the way of this solution is a good aproach.

In addition, if we need refined lattice parameters, we can try to index again by small changes from the fixed unit cell dimensions. The other way to find refined lattices parameters was given for monoclinic pattern if the pattern was indexed [15].

Furthermore, this way of solution is not convenient to explain triclinic system because it has higher unknown parameters than four. It is possible to check the other symmetry systems because they have lower unknown parameters than four.

i	Q_i(obs)	i	Q_i(obs)	i	Q_i(obs)	i	Q_i(obs)
1	0.0310	11	0.1957	21	0.3250	31	0.4083
2	0.0457	12	0.2077	22	0.3322	32	0.4432
3	0.0730	13	0.2123	23	0.3364	33	0.4450
4	0.0769	14	0.2386	24	0.3428	34	0.4498
5	0.1165	15	0.2436	25	0.3451	35	0.4608
6	0.1187	16	0.2517	26	0.3505	36	0.4659
7	0.1239	17	0.2563	27	0.3664	37	0.4768
8	0.1649	18	0.2793	28	0.3723	38	0.4863
9	0.1699	19	0.2884	29	0.3824	39	0.4918
10	0.1816	20	0.3065	30	0.4016	40	0.4938

Table 1: Q_i(obs) values of $MgWO_4$ taken from Ishida and Watanabe[11].

0.0457
0.1649
0.1816
0.2077
0.2123

Table 2: Fixed Q(h,k,0) values in Q_i(obs)'s.

S_1	S_2	S_3	S_4	N
0.0878	0.0457	0.0310	0.0923	21
0.0412	0.0457	0.0310	0.0008	21
0.0861	0.0457	0.0310	-0.0906	23*
0.1428	0.0457	0.0310	-0.1362	17
0.0646	0.0457	0.0310	0.0920	18
0.0390	0.0457	0.0310	0.0615	17
0.0236	0.0457	0.0310	0.0310	21
0.0183	0.0457	0.0310	0.0006	18
0.0232	0.0457	0.0310	-0.0299	17
0.0383	0.0457	0.0310	-0.0604	22
0.0635	0.0457	0.0310	-0.0908	19

Table 3: Some possible solution sets of S_1, S_2, S_3, S_4 carried out by the aid of N and the indexing error < 0.0005. As shown in this table, N(max)=23.

i	Q_i(obs)	h,k,l	i	Q_i(obs)	h,k,l
1	0.0310	001	21	0.3250	013
2	0.0457	010	22	0.3322	212
3	0.0730	111	23	0.3364	232
4	0.0769	011	24	0.3428	200
5	0.1165	101	25	0.3451	112
6	0.1187	121	26	0.3505	132,240
7	0.1239	002	27	0.3664	103,123
8	0.1649	220	28	0.3723	330
9	0.1699	012	29	0.3824	241
10	0.1816	020	30	0.4016	331
11	0.1957	221	31	0.4083	030
12	0.2077	210	32	0.4432	031
13	0.2123	230	33	0.4450	223,321
14	0.2386	211	34	0.4498	120,341
15	0.2436	231	35	0.4608	023
16	0.2517	111	36	0.4659	202
17	0.2563	131	37	0.4768	242
18	0.2793	003	38	0.4863	141,213
19	0.2884	222	39	0.4918	233,332
20	0.3065	022	40	0.4938	004

Table 4: The indices of all Q_i(obs)'s of $MgWO_4$ produced by fixed unit cell parameters with error < 0.0030.

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