UDC 538.911+519.688
DOI: 10.15587/1729-4061.2018.142752

DEVELOPING AND PROGRAMMING THE ALGORITHM OF REFINEMENT OF THE CRYSTAL STRUCTURE OF MATERIALS WITH POSSIBLE ISOMORPHOUS SUBSTITUTION

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В більшості випадків у програмному забезпеченні для аналізу даних Х-променевої дифрактометрії не передбачено можливості збереження стехіометричних співвідношень між хімічними елементами та співвідношень між заповненням атомами кристалографічних позицій. Тому було розроблено та програмно реалізовано алгоритм, завдяки якому у матеріалах, що допускають ізоморфне заміщення, коректно розраховується розподіл атомів за кристалографічними позиціями із збереженням стехіометричного складу. Запропоновано поєднання можливостей використання розробленого алгоритму та програми FullProf. Це дозволяє враховувати різні умови, які накладаються на розподіл атомів за кристалографічними позиціями. Запропоновано оцінку однозначності визначеного стартового розподілу атомів шляхом пошуку локальних мінімумів у певних фізично обґрунтованих межах змін параметрів структури.

Розроблено комплексний метод мінімізації функції відхилення теоретично розрахованих дифрактограм від експериментальних, який дозволяє уникати попадання цільової функції у локальний мінімум. Запропоновано два шляхи мінімізації різниці між розрахованою та експериментальною дифрактограмами. В першому за допомогою розробленого алгоритму знаходиться заповнення кристалографічних позицій, а вбудований у програму FullProf метод мінімізації обчислює всі інші параметри. В другому – використовується тільки розроблений алгоритм, а всі раніше наближені за допомогою програми FullProf параметри є зафіксованими. Показано ефективність даного алгоритму при встановленні розподілу атомів за підґратками у ферит шпінелях. Розроблений алгоритм по уточненню кристалічної структури може бути застосованим до будь-яких матеріалів, в яких можливе ізоморфне заміщення, зокрема шпінелей, гранатів, перовскитів та ін.

Ключові слова: алгоритм аналізу дифрактограм, уточнення структури, програма FullProf, структурний аналіз, твердий розчин

1. Introduction

In recent years, the growth of interest to the properties and characteristics of nano-dispersed materials has stimulated a significant surge of activity in the researching of their structure. A lot of information about the structure of materials is given, first of all, by the method of electron microscopy, electron diffraction and different spectroscopic methods. However, the most important method for establishing the crystal structure is the X-ray diffraction method, which allows the establishment of such important characteristics of nanocrystals as phase composition, parameters of the unit cell, the size of the crystalline blocks, the degree of distortion of the crystal structure, etc. [1, 2].

To analyze the diffractograms, both manual calculations and a number of commercial and free software (GSAS, MAUD, EVA, TOPAS, Jade, Fullprof, Rietan, PowderX, Powder Cell, etc.) are used. They have a lot of larger or smaller capabilities for analyzing and obtaining information from the diffractograms. The powerful analytical software that has wide functionality

for processing and analysis of X-ray diffraction data, such as Jade (MDI) or DiffracPlus (Bruker Corporation) is worth noting. This type of software provides a very high level of functionality during processing and analyzing data, and is important for everybody, who work in X-ray structural laboratories. However, this software is commercial, which greatly limits the range of researchers, who can use it. There are free or inexpensive alternatives to these commercial packages. Nevertheless, analysis of diffractograms of stoichiometric materials that allow isomorphous substitution, with the help of free software is complicated due to the limited functionality of such programs. For example, most of them, when approximating, do not use the stoichiometric principles between elements and ratios between the occupation of crystallographic positions by atoms, although in most cases only stoichiometric materials are explored.

Also, there is no analysis of the unambiguity of the results. Therefore, an actual task is the development of additional algorithms and corresponding programs for analysis of diffractograms of solid solutions and other materials, which allow isomorphous substitution.

2. Literature review and problem statement

The parameters of the microstructure of materials are determined by different authors both manually and with the help of software. For example, one of the methods for determining the distribution of cations in sublattices of the spinel structure by X-ray diffraction analysis is a comparison of the experimental and calculated values of the structural amplitudes of the F_{hkl} diffraction patterns from different crystallographic planes [3]. Finding the ratio of the integral intensities of the lines (220) and (222) (dependent on the cation distribution) to the integral intensity of the line (440) (independent of the cation distribution), one can find the distribution of atoms according to the sublattices (degree of spinel's inversion). However, this method uses only three diffraction lines, although the diffractogram contains a number of intense peaks, which carry information in varying degrees about the distribution of atoms in sublattices. Also, the use of this method is limited to two types of atoms in the sublattice. Therefore, it is necessary to use the full-profile analysis and related software.

It is worth paying attention to such a source of free software (and information about commercial software packages) for the analysis of diffraction in single crystals and powder materials, such as Collaborative Computational Project No. 14 (CCP14) [4]. Funding for the CCP14 ended in 2007, but current information is still there and a significant part of it is regularly updated. Many programs, which are archived by CCP14 have links to the most authoritative source, so the most recent versions can usually be downloaded directly from their authors. CCP14 also includes links to quite a lot of free tutorial information for analyzing different materials. Analysis of a large part of this software is presented in [5]. This software allows varying the parameters that characterize both obtaining diffractograms and sample structure. The software of this type uses both known approaches and formulas, as well as researchers' approaches to solving specific problems, and it is also usually possible to choose a particular option. Also, there are often cases where the approach in the description of the program is not specified, or only the basic data are given without details.

For a quantitative X-ray structural analysis, a full-blown Rietveld analysis [6] is widely used. In the Rietveld method, the least squares method is used to minimize the difference between the calculated and the experimental diffractograms. According to this principle, Powder Cell [7] and FullProf Suite [8] work. However, software means, which use the Rietveld method for operational analytical control are not well developed. The main reason is that the Rietveld method is based on the nonlinear least squares method, which for convergence requires a fairly accurate initial approximation of the specified parameters for each sample. Problems and difficulties that arise when using the Rietveld method are described in [9]. The difficulty and high requirements for the qualification of personnel hinder the wide expansion of this promising method, especially in industrial analytic laboratories.

In recent years, a significant part of the structures of powder substances is determined by computational stochastic methods of global optimization in direct space (Monte Carlo, annealing imitation, genetic algorithms) due to the rapid increase in computer productivity. The main method is to simulate annealing, implemented in a number of known programs (TOPAS [10], EXPO [11]). To a lesser extent, genetic algorithms are used (MAUD program [12]). Both methods are used to minimize the objective function, which, like the Rietveld method, is based on the difference between the calculated and experimental diffractograms. As in the Rietveld method, the problem of these methods is the deterioration of convergence with increasing complexity of the investigated structures.

For the solution of this problem, the works [9, 13] were carried out. In these works, the development and research of the efficiency of automated methods of full-profile X-ray structural analysis are carried out. These methods are based on the integration of the Rietveld method, genetic algorithms and parallel computing. In [13], restrictions were introduced in the form of data about the quantitative chemical composition of the sample, which greatly simplifies the search for a minimum. However, applications, which run on the above-described algorithm are not freely available, so the number of researchers, who have the ability to use the program data is very limited. Different types of restrictions that arise in solving specific diffraction problems are possible in the TOPAS program [14], but this program is commercial and not available to all researchers.

FullProf Suite is one of the largest freeware intended for the decoding of X-ray diffractograms [8]. FullProf Suite (for Windows, Linux and macOS) is based on a set of crystallographic programs (FullProf, WinPLOTR, EdPCR, GFourier, etc.), mainly developed for Rietveld' method analysis of X-ray powder diffractograms or neutrons. Various programs can be launched either in their own form (from the console window or directly in the shortcut), or from the WinPLOTR and/or EdPCR interfaces. FullProf has many features to take into account the parameters of obtaining diffractograms, diffractograms themselves and crystal structure and microstructure. Also, the advantage of this program is the ability to view and edit the input and output files. It's worth noting that FullProf involves overlaying user-defined conditions, but the functionality of the program in this direction is quite limited. In particular, there is no possibility of imposing conditions of using the stoichiometric principles in the distribution of atoms in different crystallographic positions. There is also no ability for using the ratio in the atoms occupation of various crystallographic positions.

Therefore, there are reasons to believe that the available techniques and software do not fully cover all the problems,

which arise in the structural analysis of materials. This is the reason for the need for further work in the direction of developing algorithms and their program implementation for the correct determination of the structure of materials that allow isomorphous substitution.

3. The aim and objectives of the study

The aim of the research is to refine the crystal structure of materials that allow isomorphous substitution.

To achieve this aim, the following objectives were set:

– to develop an algorithm for refining the distribution of atoms according to the crystallographic positions, taking into account the use of the stoichiometric principles for the material and assess the unambiguity of the obtained distribution;

– to develop a method for minimizing the function of many variables for finding the minimum of the function χ^2, which makes it possible to refine the distribution of atoms by crystallographic positions with using the stoichiometric principles;

– to develop the program realization of the proposed ala gorithm and to check its efficiency on model problems in the analysis of experimental diffractograms.

4. Algorithm for the refinement of the crystal structure of materials with possible isomorphous substitution

4. 1. Consideration of stoichiometry in the analysis of solid solutions

During analyzing diffractograms, the need for imposing certain conditions occurs quite often. In particular, we encounter with this during analyzing solid solutions or other materials, in which isomorphous substitution is possible. For example, significant problems arise during analyzing materials with a spinel structure. Now these materials are widely studied, and hence the distribution of elements in sublattices is an important problem. Therefore, we consider the structure of spinel in detail [15, 16].

Spinel type crystals have a cubic close-packed lattice formed by oxide ions; in the intervals between the anions there are ions of metals with a small ionic radius. Space group Fd3m. The unit cell of spinel consists of 8 identical parts (z=8). Inside the unit cell, there are two positions that metal ions can occupy. The first one is called the tetrahedral position (A-position), and the second one is the octahedral position (B-position). The lattices formed by the *A* and *B* positions are called respectively *A* and *B* sublattices in the spinel crystals and are indicated by round and square brackets respectively. In spinel crystals, ions of metals occupy 8*A* positions and 16*B* positions in one unit cell. In general, the unit cell of spinel contains 24 cations and 32 anions of oxygen, that is, their ratio is 3:4, and the ratio between the number of atoms in the tetrahedral and octahedral sublattice is 1:2. Thus, the formula of the spinel containing the metal atoms Me1 and Me2 will be written as $(Me1)[Me2_2]O_4$. Coordinates of the cations are fixed and equal to $x=y=z=0.125$ for atoms in tetrahedral positions (8a), and $x=y=z=0.5$ for atoms in octahedral positions (16d). Cations in the tetrahedrons usually do not fit in them under tight packing O^{2-}, which leads to the displacement of the four anions O^{2-} along the space diagonals of the cube. Therefore, the coordinates of oxygen anions are not fixed ($x=y=z$). For an ideal lattice, the coordinates of the anions are 0.25, but very rarely they are equal to this value in the real lattices.

So, the shape of the spinel diffractograms is influenced by both the distribution of atoms in the sublattices and the position of the oxygen atom (oxygen parameter). Therefore, during analyzing these materials, it is necessary to use a full-profile analysis and software, which could establish the conditions for stoichiometry and conditions for the distribution of atoms in crystallographic positions.

Based on the fact that among the free software, FullProf has one of the widest functionality, the ability to change the parameters and consider different approaches, this program was chosen by us for further use. As already mentioned, the principle of FullProf is based on the Rietveld method, in which the minimization of the χ^2 function is performed by the least squares method. The quality of agreement between observed and calculated diffractograms is also measured by a set of modern conditional factors R_p and R_{wp}. The first set uses all the points. In the second set, only those points where there are Bragg contributions are taken into account. However, in this program it is not possible to use the stoichiometric principles between crystallographic positions, in particular, the occupation of tetrahedral and octahedral positions by atoms in the spinel in the ratio of 1:2, and cations to anions of 3:4.

Therefore, to use all the capabilities of the FullProf program, a special program has been developed in the C++ Builder, which finds the minimum of the χ^2 function of the deviation of the theoretical diffractogram from the experimental one. The developed program in some interval carries out the sorting of the parameters of occupation of crystallographic positions by atoms and coordinates of oxygen atoms (oxygen parameter). In this case, the specified parameters are fixed. During sorting, the boundaries of all these parameters are changed and the change step is set. To reasonably determine the ranges of occupation of crystallographic positions one can also use the equations which, by the distribution of atoms in the sublattices, make it possible to compute the theoretical lattice constant (Pua equation [17] or its analogs [18–20]). In this case, the degree of deviation of the theoretically calculated constant lattice from the experimental one is set, and then the boundaries of the parameter changes are calculated. During sorting, depending on the type of task or convergence, you can use or not the minimization mechanism built-in in FullProf. If you do not want to use the built-in approximation mechanism, you can put 0 cycles in the FullProf program or fix all parameters. For a complete approximation of non-fixed parameters, you can put, for example, 20 cycles.

Regardless of the use or non-use of the approximation method built-in in FullProf, there is a problem of unambiguity of the results obtained (in the case of a spinel – the distribution of atoms according to the crystallographic positions and the coordinate of the oxygen ion). For unambiguity estimation of the parameters of the structure $p_1, p_2, ..., p_p$, we have analyzed the multidimensional surface of the dependence χ^2 on the parameters p_i. By choosing projections onto the plane $\chi^2(p_i)$, the unambiguity of the parameters determination can be estimated by the number of minima on the surface obtained. The result will be unambiguous if there is a single minimum.

The specific local minimum of the χ^2 function was chosen from certain physical considerations, a satisfactory match between theoretical diffraction patterns and experimental or additional experimental studies. To clarify the occupation parameters, a further "descent" into this minimum was carried out. As a starting point, a set of

parameters corresponding to the smallest χ^2 in this local minimum was chosen.

Therefore, although FullProf has a powerful method of minimization, in addition to the used method the method proposed by the authors of this article was used in the developed program. This method was used to reduce the probability of falling into the local minimum of the χ^2 function. Let's describe the essence of this method in more detail.

4. 2. Method of approximation of experimental diffractograms by theoretically calculated

After selecting the starting approximation, the refinement of the occupation parameters and the coordinates of oxygen atoms are made by means of a set of methods for minimizing the deviation of the theoretically calculated diffractograms from the experimental ones.

Proceeding from the fact that the approaching parameters are dissimilar, χ^2 was calculated for the new $2n$ points, where n is the number of parameters that change with finding the optimal occupation. These $2n$ points are obtained from one by one changing parameters on a given value in the direction of their increase and decrease, and taking into account the possible restrictions on the occupation parameters. Among the obtained $2n+1$ points and, respectively, the values of χ^2, the point with the smallest χ^2 was selected, which became the starting point.

This method for determining the minimum of the χ^2 function (configuration method) is effective in the case of a single minimum, but the rate of minimization with its help is rather low. However, in the process of computing by this method, χ^2 and the intensity of theoretically calculated diffractograms for all sets can be memorized, which makes it possible without additional calculation of χ^2 to use other methods for minimizing the functions of many variables. Such augment of additional methods of calculation does not significantly affect the computing time, but significantly accelerates the calculations in general. Therefore, the least squares method and the gradient method are also used to minimize the function χ^2.

The basic essence of the Gauss least squares method can be expressed in the matrix form as follows:

$$\hat{T} = \left[\left(\hat{A}^{\mathrm{T}} * \hat{A}\right)^{-1} * \hat{A}^{\mathrm{T}}\right] * \hat{Y},$$

where $\hat{\mathrm{A}}$ is the matrix consisting of numbers that are equal to the half-difference of sum deviations in one and the other side in each of the parameters, $\hat{\mathrm{A}}^{\mathrm{T}}$ is the transposed matrix, $\hat{\mathrm{Y}}$ is the matrix, whose elements are the difference between the experimental and theoretically calculated intensities of the diffracted wave at each of the angles: $\hat{\mathrm{Y}}(j)=I^E(\Delta\theta_j)-I^{\mathrm{T}}(\Delta\theta_j)$. The result of the calculations is a matrix of required parameter changes $\hat{T}$.

In the gradient method, the gradient of the function χ^2 in the n-dimensional space of the parameters of the crystal structure was determined by calculating the partial derivatives of the function χ^2 for each of these parameters:

$$\mathrm{grad}\,\chi^2 = \sum_{i=1}^{n} \frac{\partial \chi^2}{\partial p_i} \vec{i}_i,$$

where $\vec{i}_i$ is the unit vectors in the n-dimensional space of the parameters. The value χ^2 calculated previously in the configuration method was used to calculate the partial derivatives, and the direction of maximum decrease of χ^2 was memorized.

In the developed program, the combination of the three above mentioned methods was used simultaneously to determine the fill parameters. After calculating by each method, only the direction was memorized, in which the change of parameters led to the largest decrease of χ^2. The value of the change step for each of the parameters was either constant, or a given percentage of the parameter value. If all or some of the methods led to a decrease of χ^2, then the point with the minimum χ^2 becomes the starting point and the procedure is repeated. If none of the methods reduced χ^2, then the step was halved several times, and attempts were made to minimize. In the case, where χ^2 of all adjacent points is greater than the starting point, the calculations were stopped.

To accelerate the calculations, the possibility of improving the result after finding the optimal direction of χ^2 change by a certain method was envisaged – the parameters in this direction changed until χ^2 began to increase. Three or fewer obtained points, which lead to a decrease of χ^2 are compared with each other, and the starting point for the next cycle is chosen among them.

Thus, we can minimize χ^2 in two ways:

1) combining two methods (the method proposed by the authors finds occupation of crystallographic positions, and built-in in FullProf program – all other parameters);

2) using only the proposed method, fixing all the parameters that have already been approximated using the FullProf program.

5. Results of the analysis of solid solutions of stoichiometric composition on the example of ferrite-spinels

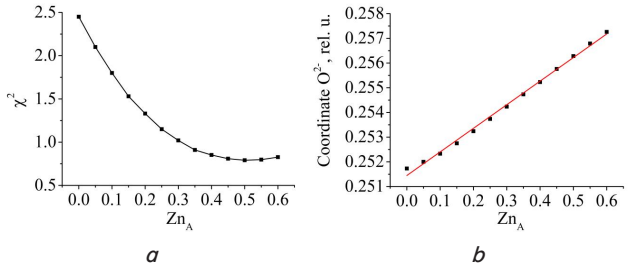
The use of the proposed algorithm is shown on the example of a spinel of the composition $Zn_{0.6}Ni_{0.4}Fe_2O_4$. Phase identification of the samples was performed using an X-ray powder diffractometer Philips PW1710 (Netherlands). The diffractograms were obtained using $Cu_{K\alpha 1}$ radiation and a graphite monochromator.

Fe ions are equally likely to occupy both tetra- and octa-sublattices. Zn ions have an advantage over the A sublattice, but under certain conditions may also be included in the B sublattice. Ni ions have an advantage over the B subgroups [21]. Therefore, it is impossible to determine correctly the distribution of ions in sublattices without imposing certain conditions even with the FullProf program.

To analyze the diffractogram, we used two programs: FullProf and the program we developed according to the algorithm described above. The determined lattice constant is equal to 0.84014 ± 0.00004 nm. At the initial distribution $(Zn_{0.60}Fe_{0.40})_A[Ni_{0.40}Fe_{1.60}]_BO_4$, the lattice constant theoretically calculated according to the Pua formula is equal to 0.8379 nm. When the content of Zn changes in the tetrahedral positions, the theoretically calculated lattice constant varies from 0.8379 nm to 0.8381 nm. These limits are too narrow to act as limitations in determining the range of changes in the Zn content in tetrahedral positions. Therefore, an analysis of the possible content of Zn in the tetrahedral positions was conducted throughout the possible range of Zn changes, that is, from 0 to 0.6. Dependences of χ^2 and coordinates of the oxygen atom on Zn_A (Zn_A – content of Zn in the tetrahedral positions) were obtained by means of sorting using the program compiled by the authors (Fig. 1). In this case, the build-in minimization mechanism in FullProf

was used for fixed parameters that characterize the distribution of atoms in the spinel sublattices. As we can see from Fig. 1, *a*, there is one minimum when the Zn content in the tetrahedral positions is equal to 0.50, that is, the distribution of atoms in sublattices is unambiguous. By selecting a point with a minimum χ^2 as the start, the described minimization method was used. As a result of minimization, the amount of Zn in the tetrahedral positions is equal to 0.57, that is, the following distribution of atoms in sublattices is obtained: $(Zn_{0.512}Fe_{0.488})_A[Zn_{0.088}Ni_{0.400}Fe_{1.512}]_BO_4$. The strong dependence of the coordinates of the oxygen atom on the distribution of zinc in sublattices (Fig. 1, *b*), which indicates the sensitivity of this parameter to cation distribution is worth noting. The coordinate of oxygen, obtained in approximation, is x=0.2564.

The degree of approximation of the theoretically calculated diffractogram to the experimental is shown in Fig. 2. The proximity of experimental data and data, theoretically calculated based on the developed algorithm, testifies to the adequacy of the proposed approximation and the effectiveness of the proposed algorithm. The obtained distribution of cations in sublattices for this spinel is confirmed by other methods of investigation, in particular by Mossbauer spectrometry.



a *b*

Fig. 1. Dependences on the Zn content in the tetrahedral positions: a – χ2, b –oxygen ion coordinates

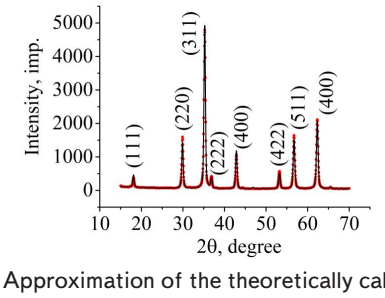


Fig. 2. Approximation of the theoretically calculated diffractogram of the spinel (black line) to the experimental (red point)

In addition, a good agreement between the distribution of cations in sublattices obtained by this algorithm and distributions obtained by other methods is also observed for other systems: $Li_{0.5}Fe_{2.5-x}Al_xO_4$ [22], $MgCr_xFe_{2-x}O_4$ [23], $Mg_{1-x}Zn_xFe_2O_4$ [24], $Ni_{1-x}Cd_xFe_2O_4$ [25], $Ni_xCo_{1-x}Fe_2O_4$ [26], $NiCr_xFe_{2-x}O_4$ [27], $Zn_{1-x}Co_xFe_2O_4$ [28].

6. Discussion of the results of implementation of the algorithm for refining the structure of materials

During calculating the cation distribution of atoms between the crystallographic sublattices, an ambiguity in the given distribution may arise. This is due to the fact that the intensity of the lines on diffractograms affects both the type of atom in a crystallographic position and its position. In particular, in the structure of the spinel, the intensity of the diffraction lines is determined by the distribution of atoms between the tetrahedral and octahedral positions, as well as the coordinates of the oxygen ion.

Although Fig. 1 shows the case of unambiguous determination of the distribution of atoms in sublattices, it is possible to compensate for the mutual influence of the distribution of atoms in sublattices and the position of the oxygen atom. Then the determining factor in choosing a local minimum is the use of other methods of researching the distribution of atoms in sublattices. As an example, the use of the Mossbauer spectroscopy makes it possible to determine the ratio of the number of iron ions in the octahedral sublattice to the number in the tetrahedral sublattice. However, this important information cannot be used in the FullProf program or in other commonly used free software. The use of the proposed algorithm and its software implementation allows you to take into account all available sample information.

Ambiguity in the obtained approximated parameters is possible not only when determining the distribution of atoms in the sublattices. As the authors of FullProf say in the user manual, although the principles underlying the Rietveld profile refinement method are rather simple, the use of the technique requires some experience. This results merely from the fact that Rietveld refinement uses a least-squares minimization technique, which, as any local search technique, gets easily stuck in false minima. Besides, the correlation between model parameters, or a bad starting point, may easily cause a divergence in early stages of the refinement. Also in the explanation to the program, it is said that all these difficulties can be easily overcome while complying with the recommendations given in the program explanation.

However, with the practical use of FullProf, there is often a divergence when using approximation. On the one hand, the divergence is a quick and effective method for detecting errors in the model or in the input file that controls the refinement process. On the other hand, when large and unreal fluctuations of some parameters occur from one cycle to the next, separate individual parameters need to be clarified, at least in the early stages of refinement.

The use of the algorithm proposed in this article in many cases makes it possible to avoid the described situation by adjusting the step of changing specific parameters. The ability to change the step of changing the parameters also leads to a better descent into the minimum of the function χ^2.

It is worth noting that the use of different restrictions on the values of approaching parameters can lead to a deterioration of the quality of approximation. The absence of any constraints on the model parameters often leads to a "good look" of the approximate diffractograms and small χ^2, but the obtained parameters do not have physical content and often describe non-existent situations. Therefore, during approximation, it is necessary to critically evaluate the contents of all parameters. Also to take into account that the diffractogram can be from a sample that is not described by the model of crystal structure and microstructure, used in the program. In addition, it should be borne in mind that imposed restrictions also have their own accuracy and limits of application.

This algorithm for refining the crystal structure can be applied to any materials in which isomorphous substitution is possible, in particular spinels, garnets, perovskites, and others.

The idea of the described algorithm can also be used in other free software, which considers the approximation of experimental data by theoretical. Also, this algorithm can work as a separate program for data analysis, where it is necessary to approximate discrete data by the function.

7. Conclusions

1. An algorithm and its program implementation are developed for refinement of the crystal structure of materials with possible isomorphous substitution. The combination of using the developed program and the free FullProf program is proposed. This allows taking into account various conditions, which are imposed on the distribution of atoms by the crystallographic positions. At the same time, in order to determine the initial distribution of atoms by the crystallographic positions, in certain physically substantiated boundaries, the search for local minimum is carried out. This process simultaneously can be used for estimation of the unambiguity of the determined atomic distribution.

2. The combination of the developed complex of methods of minimization and method of minimization built-in in FullProf is proposed for the detailing of the distribution of atoms by the crystallographic position. Due to such combination, falling of the function of the deviation of theoretically calculated diffractograms from the experimental ones to a local minimum can be avoided.

3. Effectiveness of the developed algorithm is illustrated in determining the distribution of atoms in the sublattices of ferrite-spinels using stoichiometric principles in the occupation of crystallographic positions. The obtained distribution of atoms is agreed with the distribution obtained by the method of Mossbauer spectrometry that gives grounds to assert the correctness of the developed algorithm.

Acknowledgments

The authors express their gratitude to Hanna Yaremii for the help in designing and translating the article.

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