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X-ray structural analysis of multicomponent oxide powders with a pyrochlore structure using the Rietveld method: features, techniques, limitations

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A set of techniques for analyzing multicomponent oxide powders with a pyrochlore structure using the Rietveld method was developed, which allows for precise refinement of the compounds composition in the presence of atoms of different sorts in each of two structurally non-equivalent crystallographic positions (A and B). The developed method was tested using the example of the $Bi_2O_3-Na_2O-Fe_2O_3-WO_3$ system and made it possible to determine the precise composition of a compound with a pyrochlore structure in a sample obtained by hydrothermal synthesis — $(Bi_{1.08}Na_{0.08}\square_{0.84})(Fe_{0.44}W_{1.56})O_7$, where $\square$ — cation vacancy.

Keywords: multicomponent oxides, pyrochlore structure, X-ray structural analysis of powders, Rietveld method.

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Complex oxides with pyrochlore structure show a set of important physical and chemical properties, which include magnetic, transport, photocatalytic and other properties. Pyrochlore structure ($A_{2-x}B_2O_6O'_{1-\delta}$) is built by two mutually penetrating sublattices A_2O' and B_2O_6. Position A is occupied by cations $Me^{1+,2+,3+}$ of relatively large radius, whereas cations $Me^{4+,5+,6+}$ of smaller radius are placed in position B. Cations $Me^{2+,3+}$ of relatively small radius are located mostly in position B. Precise definition of chemical composition of multicomponent pyrochlores using Rietveld method is a non-trivial problem: it is necessary to refine the occupation of the positions, where atoms of various sorts and vacancies may be present at the same time.

The aim of this paper is the development of the method of refinement of the composition of multicomponent pyrochlores by Rietveld method. A model object is pyrochlore in the $Bi_2O_3-Na_2O-Fe_2O_3-WO_3$ system produced by hydrothermal synthesis method [1].

Bulk chemical composition of the sample in the form of atomic ratios was determined on scanning-electron microscope Tescan Vega 3 SBH with Oxford Instruments attachment for energy-dispersive X-ray analysis (EDX): Bi/W = 0.81(2), Fe/W = 0.53(1), Bi/Fe = 1.53(3) and Na/W = 0.06(1). Powder X-ray diffraction (XRD) pattern of the sample was obtained at room temperature using X-ray diffractometer Rigaku SmartLab 3 (Bragg−Brentano geometry, Cu-K_α radiation of X-ray tube with Cu anode, Ni K_β-filter, $2\theta-\theta$ scanning mode). The preliminary analysis of the diffraction pattern was carried out to determine parameter a of cubic unit cell of pyrochlore using Bragg angles $2\theta_B$ of reflections and their Miller indices hkl and parameters of microstructure (average size D of crystallites (areas of coherent scattering of X-rays) and absolute values of average microstrains ε_s in them) by graphical methods of Williamson−Hall plot (WHP) and „Size−Strain“ plot (SSP) taking into account the pseudo-Voigt (pV) type of observed reflections. Le Bail (LB) method and Rietveld method were used with TOPAS software, v. 5 (Bruker AXS, Germany). Detailed description of X-ray measurements, preliminary analysis and processing of X-ray diffraction patterns, the procedure of using LB and Rietveld methods, and used software is provided in papers [1,2].

Powder XRD pattern of the sample contains a set of rather narrow reflections, which belong to the phase of cubic syngony with pyrochlore structure [1]. The results of preliminary analysis of structural and microstructural parameters of pyrochlore are given in Table. Both graphical methods, WHP (Figure 1, a) and SSP (Figure 1, b), yield similar results: broadening of reflections is mainly due to the presence of microstrains in crystallites of „infinite“ (submicron) size.

The pyrochlore values a, D and ε_s obtained in this manner were used as start ones for full-profile LB fitting (see Table). Two amorphous halos (with centers at $2\theta \approx 25.6$ and $52.5°$, relative maximum intensities $I_{\max} \sim 0.7$ and 0.3%, accordingly, and full width at half

Table. Final microstructural (D and ε_s) and structural (a; x, y, z; B_{iso}; p and q (summary coefficient of occupancy for close equivalent positions)) parameters obtained in profile analysis of XRD reflections by graphical methods of WHP and SSP, and also in refinements by LB and Rietveld methods for pyrochlore phase (space group $Fd\bar{3}m$ (227), setting 2) in the $Bi_2O_3-Na_2O-Fe_2O_3-WO_3$ system. Besides, values of average criteria $FWHM/B_{int}$ of the type of observed reflections are indicated (pV-type), as well as coefficients of determination R_{cod} for WHP and SSP plots, and agreement factors (R_{wp} and R_B) for LB and Rietveld methods. Other designations are given in the text and in the captions to figures

<table>
<tr><td rowspan="2" colspan="4">Profile analysis of XRD reflections: $a = 10.36836(10)$ Å,
reflections of pV-type: $FWHM/B_{int} = 0.75(7)$</td><td colspan="2">WHP ($R_{cod} = 73.88\%$)</td><td colspan="2">$D = 1876\,\text{nm}^{a,b}$,
$\varepsilon_s = 0.057(6)\%^{b}$</td></tr>
<tr><td colspan="2">SSP ($R_{cod} = 0.58\%$)</td><td colspan="2">$D = \infty^{b}$,
$\varepsilon_s = 0.057(10)\%^{b}$</td></tr>
<tr><td colspan="8">Refinement by LB method: $a = 10.36867(7)$ Å, $D = 608(24)\,\text{nm}^{b}$, $\varepsilon_s = 0.0543(5)\%^{b,c}$, $R_{wp} = 3.096\%$, $m_{e.s.d.} = 4.819^{d}$</td></tr>
<tr><td colspan="8">Refinement by Rietveld method: $a = 10.36866(8)$ Å, $D = 627(32)\,\text{nm}^{b}$, $\varepsilon_s = 0.0541(5)\%^{b,c}$,
$R_{wp} = 3.169\%$, $R_B = 0.510\%$, $m_{e.s.d.} = 5.288^{d}$</td></tr>
<tr><td>Atom</td><td>Wyckoff position</td><td>x</td><td>y</td><td>z</td><td>p</td><td>q</td><td>B_{iso}, Å^2</td></tr>
<tr><td>Bi</td><td>96g</td><td>0.4785(6)</td><td>0.5163(4)</td><td>y</td><td>0.0902(4)</td><td>0.541(2)^{e}</td><td>1.63(9)</td></tr>
<tr><td>Na</td><td>96g</td><td>x_{Bi}</td><td>y_{Bi}</td><td>y_{Bi}</td><td>0.007(3)</td><td>0.042(16)^{e}</td><td>$B_{iso\,Bi}$</td></tr>
<tr><td>W</td><td>16c</td><td>0</td><td>0</td><td>0</td><td>0.779(4)</td><td>0.779(4)^{e}</td><td>1.55(4)</td></tr>
<tr><td>Fe</td><td>16c</td><td>0</td><td>0</td><td>0</td><td>0.221(4)^{f}</td><td>0.221(4)^{e}</td><td>$B_{iso\,W}$</td></tr>
<tr><td>O_1 (O)</td><td>48f</td><td>0.3130(10)</td><td>1/8</td><td>1/8</td><td>1</td><td>1</td><td>0.2(4)</td></tr>
<tr><td>O_2 (O′)</td><td>8b</td><td>3/8</td><td>3/8</td><td>3/8</td><td>1.00(1)^{g}</td><td>1.00(1)</td><td>10(2)</td></tr>
</table>

Note. [a] Estimated standard deviation (e.s.d.) is not indicated, since it is higher than the obtained value D.

[b] The calculations used coefficients $K_{Scherrer} = 0.94$ and $K_{strain} = 4$ for Scherrer and Wilson–Stokes equations corresponding accordingly to the contributions of full width at half maximum (FWHM)-components to broadening of reflections due to the crystallite size and microstrain value, see [1,2].

[c] Value ε_s is related to value e_0, obtained in refinements using LB and Rietveld methods by TOPAS software, as $\varepsilon_s(\%) = 2e_0 \cdot 100\%$.

[d] All e.s.d. values, received in the refinements by LB and Rietveld methods, are corrected for underestimation due to serial correlations by multiplying on coefficient $m_{e.s.d.}$, calculated using Bérar procedure, see [2].

[e] For Bi and Na atoms in position A 96g (x, y, y), atoms are distributed over six close equivalent positions, therefore $q = 6p$ — summary occupancy coefficient of six close equivalent positions A, where atoms Bi and Na may be located ($0 \leq q \leq 1$). In case of W and Fe atoms located in position B, $q = p$ — coefficients of occupation of this position with W and Fe atoms, accordingly ($0 \leq p \leq 1$).

[f] Calculated as $p_{Fe} = 1 - p_W$.

[g] Calculated based on principle of electroneutrality, assuming ion charges: Bi^{3+}, Na^{1+}, W^{6+}, Fe^{3+} and O^{2-}.

of intensity maximum (FWHM) ~ 8.5°) were described by refinement of parameters of pV-type wide reflections, which were treated as an additive to the background described by Chebyshev polynomial of order 6 with a hyperbolic additive. For better fitting of XRD pattern, three non-identified weak reflections (with Bragg angles $2\theta_B = 21.13$, 23.98 and 24.71°) were set as pV-type reflections, and their parameters were refined. The final achieved value of weight profile factor of agreement was $R_{wp} = 3.096\%$.

Pyrochlore values a, D and ε_s obtained as a result of the full-profile fitting by LB method were used as start ones for refinement of the pyrochlore structure by Rietveld method. One of structural models from [3] (space group $Fd\bar{3}m$ (227), setting 2) with Bi and O atoms in positions A 96g (x, y, y) and O′ 8b (3/8, 3/8, 3/8), accordingly, was taken as the start coordinates of pyrochlore structure atoms. It was assumed that position B 16c (0, 0, 0) was occupied without vacancies by W^{6+} and Fe^{3+} cations (according to obtained data of Mössbauer spectroscopy), there are no vacancies on position O 48f (x, 1/8, 1/8), and in position A apart from cations Bi^{3+} there are vacancies, and cations Na^+ may be present. Occupation of position O′ was calculated using the principle of electroneutrality from the obtained occupations of cation positions (provided that the occupancy coefficient $p_{O'} \leq 1$). The key method that made it possible to precisely refine the occupation of positions A and B with atoms of various sorts, was the alternating variation of these occupations in a manual mode when all non-structural and structural parameters were refined, and plotting of dependencies of the weight profile factor of agreement R_{wp} on the given coefficients p of position occupancy. Using the minimum of the dependence $R_{wp}(p)$, which has the characteristic form of a parabolic function, the occupancy of the analyzed position was determined on each cycle. Further this obtained coefficient p of position occupation was additionally refined (changing only slightly) and was fixed in the next cycle when constructing the curve $R_{wp}(p)$ for another position. Such refinement cycles were repeated until the occupations stopped changing within the limits of the e.s.d. Previously [2] such method

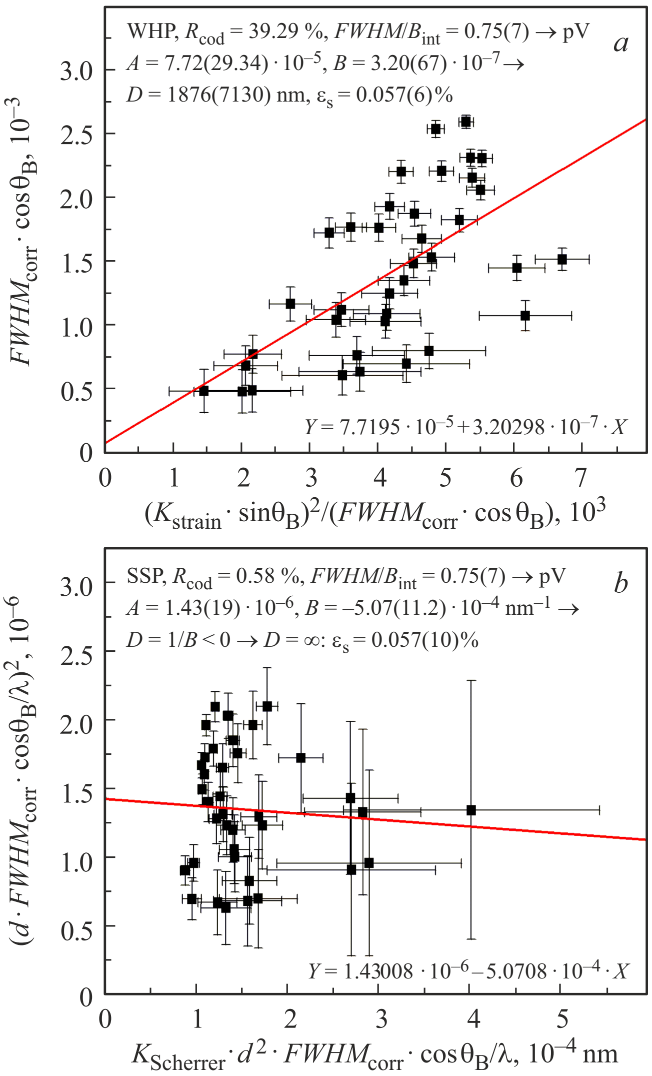

Figure 1. (*a*) WHP and (*b*) SSP graphs plotted for reflections of pyrochlore phase using procedures for reflections of pV-type (see [1]). Approximation curves $Y = A + BX$ are shown in (*a*) and (*b*), where analytic expressions for values Y and X are specified, accordingly, in the captions to the x and y axes. Symbol d means interplanar distance corresponding to a reflection with Miller indices *hkl* and Bragg angle $2\theta_B$ (values $2\theta_B$ are adjusted by angular corrections for detector zero shift and displacement of sample surface from focal plane of diffractometer), $FWHM_{corr}$ — observed FWHM of the reflection corrected for instrumental broadening using the procedure for the observed pV-type of reflections, $\lambda = 1.540598$ Å — wavelength Cu-$K_{\alpha 1}$ of radiation (after correction of Cu-$K_{\alpha 2}$ contribution). Other symbols are explained in the text. $FWHM$ and B_{int} — observed FWHM of the reflection (without corrections) and integral width of the reflection accordingly.

of constructing the curves $R_{wp}(p)$ made it possible to successfully obtain the composition of ferroelectric-relaxor $PbNi_{1-x}Ta_xO_{3-\delta}$, where heavy atoms Ta ($Z = 73$) and light atoms Ni ($Z = 28$) are in the same crystallographic position.

At the first stage of refinement it was assumed that for the occupations of cation positions A and B the ratios found by analysis with EDX method were met: $q_{Bi}/q_W = 0.81$, $q_{Fe}/q_W = 0.53$ and $q_{Na}/q_W = 0.06$, and at the same time $p_{Fe} = 1 - p_W$. Therefore, at the first stage the only variable parameter of occupancies was the occupation coefficient p_W of position B with atoms W, the optimal value of which ($p_W = 0.6536$) was obtained from the minimum of the parabolic function that describes dependence $R_{wp}(p_W)$. Variation of p_W started from the value defined by ratio $q_{Fe}/q_W = 0.53$ according to EDX results, with the subsequent cancellation of this ratio and changing value p_W manually. $R_{wp} = 3.272\%$ was achieved at this stage (and Bragg factor of agreement $R_B = 0.649\%$).

At the second stage of refinement the ratio q_{Bi}/q_W=0.81 was cancelled, but condition $q_{Na} = 0.06 \cdot q_W$ remained. In the first cycle of the second stage of refinement, the optimal value p_W, found at the first stage, was fixed, and value p_{Bi} was changed manually for the position A, and dependence $R_{wp}(p_{Bi})$ was built (Figure 2, *a*), approximated by parabolic function, the minimum of which provided optimal value p_{Bi}, which was additionally refined upon the cycle completion. In its turn, in the second cycle the value p_{Bi}, which was found in the first cycle, was fixed and the value p_W was varied manually while obtaining the dependence $R_{wp}(p_W)$ again and repeating all steps described for the first cycle. The same procedure was repeated until the values of the occupation coefficients p_W and p_{Bi} stopped changing with accuracy of up to e.s.d. ($N = 7$ cycles). The limit values y_0, obtained from approximation of dependences $p_{Bi}(N)$ and $p_W(N)$ using exponential decay law (Figure 2, *b*, *c*), were set and refined again, slightly changing. The obtained values of occupation $p^{opt}_{Bi} = 0.08972$ and $p^{opt}_W = 0.7736$ were optimal under the condition that atomic ratio Na/W is correspondent to EDX results. $R_{wp} = 3.170\%$ was achieved at this stage ($R_B = 0.516\%$).

At the final stage of refinement the final value of content Na^+ and cation vacancies in position A were determined. Values p^{opt}_{Bi} and $p^{opt}_{Na} = (0.06 \cdot p^{opt}_W)/6$ obtained provided that the atomic ratio Na/W meets EDX results, were recalculated to value p^{obs0}_{Bi} in the assumption of only atoms Bi in position A, scattering in the same manner as atoms Bi and Na with these occupation coefficients:

$$p^{obs0}_{Bi} = \frac{p^{opt}_{Bi} Z_{Bi} + p^{opt}_{Na} Z_{Na}}{Z_{Bi}}, \qquad (1)$$

where $Z_{Bi} = 83$ and $Z_{Na} = 11$ — atomic numbers of Bi and Na. This expression is an approximation and follows from the expression of the structural amplitude for position A. Using value $p^{obs0}_{Bi} = 0.09587$ as a start one for Bi atom occupation of position A in the model, where Na is absent in this position, dependence $R_{wp}(p_{Bi})$ was plotted, as it was described above, from the minimum of the approximating parabolic function of which the optimal

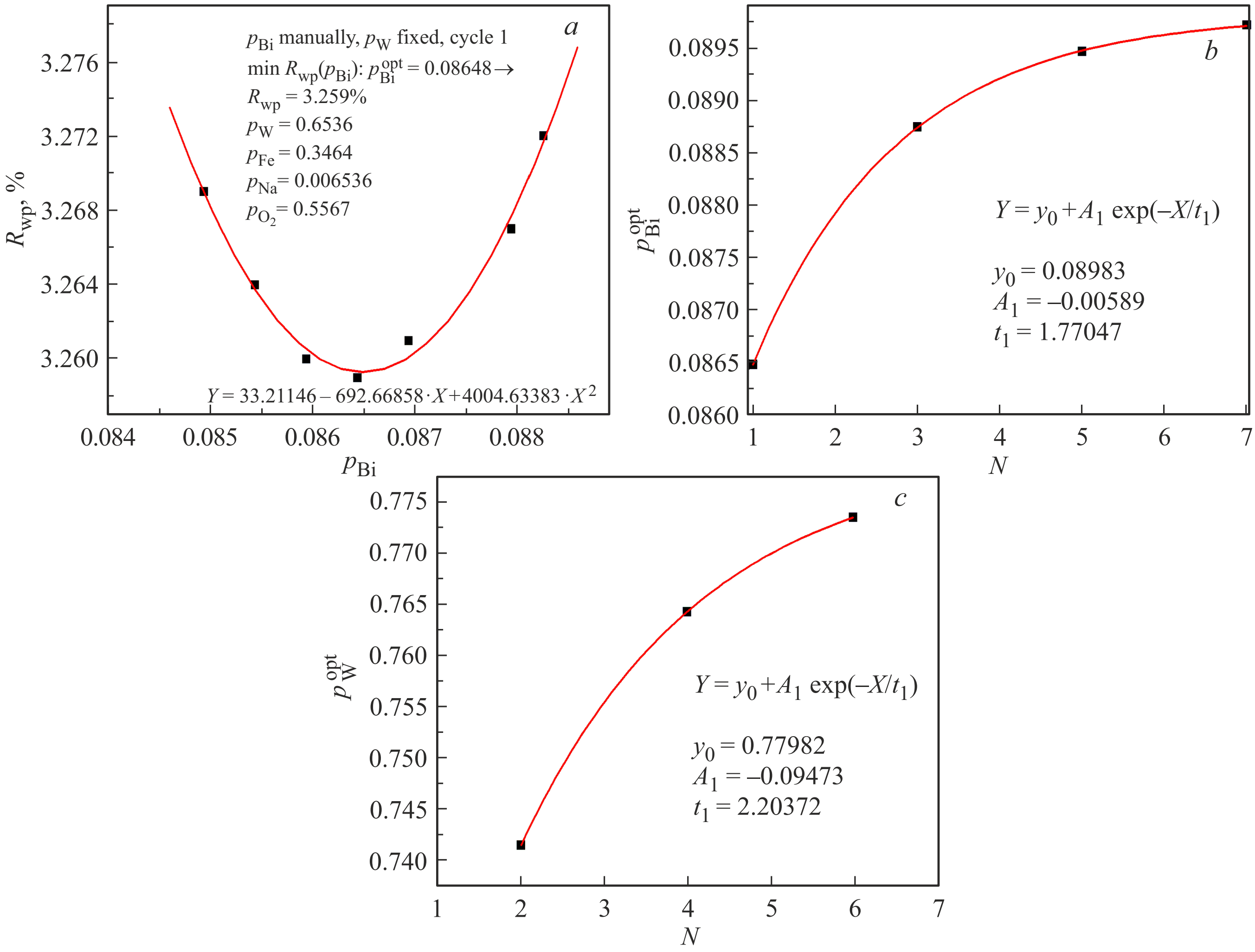

Figure 2. Dependence of weight profile factor R_{wp} on occupation coefficient of position A 96g with atoms Bi (p_{Bi}) in cycle $N = 1$ of the second stage of refinement under variation of p_{Bi} manually (a). Dependences of optimal values of occupation coefficients (b) $p_{\mathrm{Bi}}^{\mathrm{opt}}$ and (c) $p_{\mathrm{W}}^{\mathrm{opt}}$, obtained from minima of $R_{\mathrm{wp}}(p)$, similar to the one shown in (a), on the number of refinement cycles (N), where these optimal values were obtained. (a) shows the formula of parabolic approximating function, where $Y = R_{\mathrm{wp}}$, and $X = p_{\mathrm{Bi}}$. (a) shows the values of coefficients of occupation of all positions with atoms, obtained for optimal value $p_{\mathrm{Bi}}^{\mathrm{opt}}$, corresponding to the minimum of $R_{\mathrm{wp}}(p)$. (b, c) shows coefficients y_0, A_1 and t_1 of the approximating function of exponential decay $Y = y_0 + A_1 \exp(-X/t_1)$, where $Y = p_{\mathrm{Bi}}^{\mathrm{opt}}$ or $p_{\mathrm{W}}^{\mathrm{opt}}$ on (b) and (c), accordingly, and $X = N$.

„apparent" value $p_{\mathrm{Bi}}^{\mathrm{obs}} = 0.0911$ was found in the model, when scattering of Bi and Na atoms in position A was described by scattering of Bi atoms only. Final optimal values of position A occupation with Bi and Na atoms were obtained from minimum of approximation of dependence $R_{\mathrm{wp}}(p_{\mathrm{Bi}})$, obtained upon variation of value p_{Bi} provided that the total scattering by atoms Bi and Na is the same as in the case of description of this scattering only with Bi atoms:

$$p_{\mathrm{Na}} = \left(p_{\mathrm{Bi}}^{\mathrm{obs}} - p_{\mathrm{Bi}}\right) \frac{Z_{\mathrm{Bi}}}{Z_{\mathrm{Na}}}. \tag{2}$$

Final values of structure and microstructure parameters of pyrochlore crystalline phase ($R_{\mathrm{wp}} = 3.169\%$, $R_{\mathrm{B}} = 0.510\%$), obtained when refined by Rietveld method, are summarized in the Table. Graphic results of the final fitting of the simulated XRD pattern are given in Figure 3. The described method made it possible to determine the composition of the crystalline pyrochlore phase $(\mathrm{Bi_{1.08}Na_{0.08}\square_{0.84}})(\mathrm{Fe_{0.44}W_{1.56}})\mathrm{O_7}$, where $\square$ is cation vacancy. When comparing the pyrochlore composition with the bulk composition of the sample obtained by EDX method, it can be assumed the presence of X-ray amorphous phase of the composition $(\mathrm{Bi_{1.89}Na_{0.18}})\mathrm{Fe_{4.05}O_9}$ in the sample, which is close to the composition of the known compound $\mathrm{Bi_2Fe_4O_9}$. However, it should be noted that, due to the limited accuracy of EDX method in case of powder analysis, the X-ray amorphous phase composition requires further investigation.

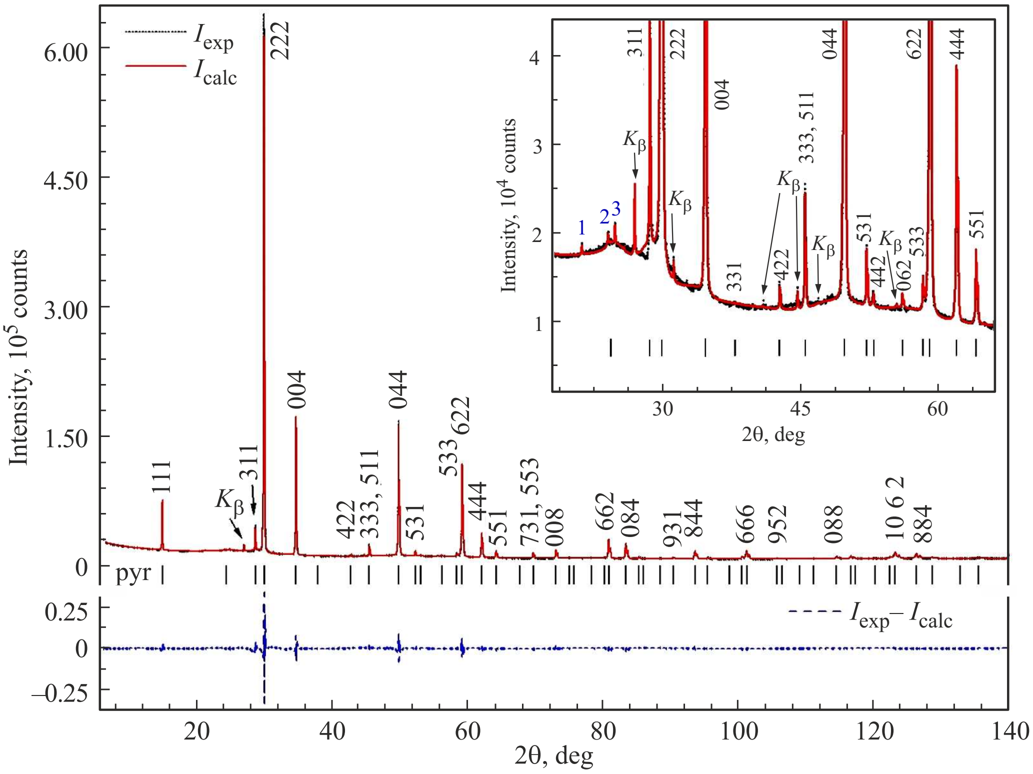

Figure 3. Final graphic results of Rietveld fitting of simulated XRD pattern to experimental one ($2\theta = 6-140^\circ$ with a step of $\Delta 2\theta = 0.01^\circ$, the total time in point 2560 sec (recalculation from the used linear detector to point detector)). The insert shows the range of diffraction angles $2\theta = 18-66^\circ$ in the increased scale. Miller indices *hkl* of the selected pyrochlore reflections are indicated. Positions of the non-identified reflections are indicated by numeric characters. Reflections due to residual K_β radiation are also indicated.

Conflict of interest

The authors declare that they have no conflict of interest.

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