X-ray diffraction investigations of the thermal expansion of iron borate FeBO$_3$ crystals

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Abstract. The lattice parameters $a$, $c$ of iron borate FeBO$_3$ polycrystals have been measured in the temperature range 25–600˚C by the X-ray diffraction method. The thermal expansion coefficients $\alpha$ are calculated from the measured values of the parameters. A substantial anisotropy of the thermal expansion is found. It is shown that the thermal expansion coefficient $\alpha_c$ along the $c$ axis is greater than the thermal expansion coefficient $\alpha_a$ in a plane perpendicular to this axis. By X-ray peak profile analysis the crystallite size was estimated from Scherrer’s formula. We have also investigated the temperature dependence of crystallite size in FeBO$_3$.

1. Introduction
Iron borate FeBO$_3$ is a model object for research in solid state physics as a result of the unique combination of a number of physical properties, such as transparency in the visible region and magnetic ordering et al. [1, 2]. The performance characteristics of iron borate are highly dependent on temperature. Under the influence of the temperature there are changes in the phase composition of the samples, in the structural characteristics of the crystal lattice, in crystallite size, etc. For example, in FeBO$_3$, heated to temperatures of about 700-800˚C there are new phases: hematite Fe$_2$O$_3$ and iron oxoborate Fe$_3$BO$_6$, [3].

The aim of this work: a study of structural and disperse characteristics of iron borate FeBO$_3$ on temperature.

2. Object and method of research
Iron borate has a calcite structure with the point group symmetry $\bar{3}m$ ($D_{3d}$) and the space group $\text{R}3\text{c}$ ($D_{3d}^6$). The space group has an R-type Bravais lattice; thus, the unit cell parameters can be specified in both hexagonal and rhombohedral settings. The structural rhombohedral parameters: $a_r=5.52$ Å, $c_r=49.54^\circ$, $V_r = 89.322\text{Å}^3$. The structural hexagonal parameters: $a_h=4.626(1)$ Å, $c_h=14.496(6)$ Å, $V_h = 268.596\text{Å}^3$, [4]. The rhombohedral and hexagonal FeBO$_3$ unit cells contain two and six formula units, respectively. Oxygen atoms surround each iron atom forming a slightly distorted [FeO$_6$] octahedron whose O atoms belong to different [BO$_3$] units [5]. The boron atoms are located in the center of plane of equilateral oxygen triangles. The borate groups are distributed in layers in such a way that the triangular [BO$_3$] groups present reversed orientations in alternating layers; while [FeO$_6$] octahedron share corners with other six octahedra: three from the upper layer and three from the lower layer, figure 1.
Figure 1. The hexagonal unit cell of the FeBO$_3$. An [FeO$_6$] octahedron is represented in green. Fe, B, and O atoms are represented as green, yellow and red spheres, respectively.

For structural studies, samples of polycrystalline iron borate were ground into powder by standard technology. The temperature behavior of FeBO$_3$ have been determined in situ by high-temperature powder X-rays diffraction method (SmartLabRigaku, CuK$_\alpha$) in the temperature range from 25°C to 600°C. The XRD investigation of FeBO$_3$ was performed in the range $2\theta = 20°$ - $100°$ in steps $h(2\theta)$=0.02°, figure 2.

Figure 2. Observed X-ray powder diffraction patterns for FeBO$_3$ at 25 °C and 600 °C.

3. Analysis and discussion
The structure parameters of FeBO$_3$ were determined according to Bragg’s law, [6]:

$$n\lambda = 2d \sin \theta$$

where $n$ - order of diffraction,
λ - X-ray wavelength,
\(d\) - interplane distance,
\(θ\) - Bragg’s angle.

The plane spacing \(d\) is related to the lattice constants \(a\), \(c\) of hexagonal structure by the following relation, [5]:

\[
\frac{1}{d_{kl}^2} = \frac{4}{a} \left( \frac{h^2 + k^2 + l^2}{c^2} \right)
\]

were \(h\), \(k\) and \(l\) - Miller indices.

The unite cell parameters calculated on the program [7] as a function of temperature are shown at table 1.

| \(t\), °C | \(a\), Å | \(c\), Å | \(V\), Å³ |
|----------|---------|---------|---------|
| 25       | 4,6285±0,0003 | 14,4878±0,0011 | 268,790±0,03 |
| 400      | 4,6620±0,0008 | 14,6313±0,0011 | 275,411±0,03 |
| 500      | 4,6642±0,0003 | 14,6445±0,0011 | 275,910±0,03 |
| 600      | 4,6691±0,0003 | 14,6544±0,0014 | 276,681±0,03 |

The dependence of the lattice constants and volume of cell on temperature has been expressed by polynoms of second order, the respective coefficients being found by the least-squares method, figure 3.

The full fit of the data to a second-order approximation:

\[a(t) = a_0 + a_1 \cdot t + a_2 \cdot t^2\]

were \(a_0\) - lattice constants at 0 °C,
\(a_1, a_2\) - characteristic constants,
\(t\) - temperature in °C.

The values of characteristic constants determined by least-squares method are shown in table 2.

| Parameter | \(a_0\) | \(a_1\) | \(a_2\) |
|-----------|---------|---------|---------|
| \(a\), Å  | 4,6255  | 1,2290·10^{-4} | -8,5442·10^{-8} |
| \(c\), Å  | 14,4740 | 5,6931·10^{-4} | -4,4978·10^{-7} |
| \(V\), Å³ | 268,189 | 0,0250 | -1,835·10^{-5} |
With respect to the definition of the coefficient of the thermal expansion, [6]:

\[ \alpha = \frac{1}{a_0} \frac{da}{dt} \]  

(4)

were \( da \) – difference of lattice parameters \( a \) for the interval \( dt \),
d\( dt \) - difference of temperature
we obtain from (3) the dependence of thermal expansion coefficient on temperature:

\[ \alpha(t) = a_1 + a_2 \cdot t \]  

(5)

The results of similar fits to obtain the linear thermal expansion coefficients of the two axes of the unite cell together with the resulting of volume thermal expansion, \( a_1 \) and \( a_2 \) are shown in table 3.

**Table 3.** Linear and volumetric thermal expansion parameters for FeBO₃.

| Coefficients | \( a_1 \) | \( a_2 \) |
|--------------|----------|----------|
| \( a_\alpha \) | 2.6571 \times 10^{-5} | -3.6943 \times 10^{-8} |
| \( a_c \) | 3.9333 \times 10^{-5} | -6.2151 \times 10^{-8} |
| \( a_T \) | 9.3255 \times 10^{-5} | -1.3683 \times 10^{-7} |

It can be seen that the thermal expansion is anisotropic, being greatest for the c-axis (i.e. for the direction along the axis of the 3-order symmetry) and smallest for the direction perpendicular to the c-axis, e.g. \( a_c = 8.0995 \times 10^{-6} \) C⁻¹ and \( a_\alpha = 8.2575 \times 10^{-6} \) C⁻¹ for \( \Delta t = 200 \) °C (400 °C – 600 °C).

The three-dimensional thermal expansion diagrams of FeBO₃ drawing according to [8] is shown in figure 4.

**Figure 4.** Indicatory surface of thermal expansion of FeBO₃.

We have investigated the parameters of the micro-structural quantities in FeBO₃ by X-ray peak profile analysis. The approximation method was used to study the individual contributions of crystallite sizes and lattice strain on the peak broadening of FeBO₃. The results showed that the diffraction peaks broadening inversely proportional to the cosine of the reflection angle caused by size of particles of crystals, [9].

We have estimated the coherent crystallite size \( (D) \) on the Debye–Scherrer equation, [10]:

\[ D = \frac{K \lambda}{B_hk_l \cos \theta} \]  

(6)

were \( K \) - constant equal to 0.90,
\( \lambda \) - wave length of the incident X-ray,
B - the width of the diffraction peak, in radians, at a height half-way between background and the peak maximum, 

θ - Bragg’s angle.

The temperature dependence of average crystallite size was calculated from XRD peak width of (102) are shown in figure 5.

4. Conclusion
In this paper we report the experimental study of the thermal behavior of iron borate FeBO$_3$ by X-ray diffraction measurements and calculations. Correct evaluations of the thermal expansion coefficients could be done in the temperature range from 400 to 600°C, since below Neel point $T_N = 75°C$, FeBO$_3$ is an easy plane weak ferromagnet with the anomalous temperature variation of the thermal expansion near the phase transition temperature [1]. Our results show that the thermal expansion of FeBO$_3$ along the c axis is more than along the a axis at temperatures above $T_N$.

It was found that the sample temperature increase leads to a monotonic and quite a substantial increase in the value of coherent crystallite size, indicating that the ordering of crystal structure in iron borate with heat processing.

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