



Conference Paper

Orientation Dependence of the Thermal Expansion Coefficients of Iron Borate FeBO_3 Crystals

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Abstract

We present high-resolution X-ray diffraction measurements of the lattice parameters of iron borate FeBO_3 . These measurements were performed at room temperature and at various temperatures ranging from 400 up to 600°C, enabling the determination of the coefficients of thermal expansion (CTE). The three-dimensional (3D) indicatory surface of thermal expansion of FeBO_3 was constructed in MathCad. It is shown that the orientation dependence of CTE in FeBO_3 is spheroid elongated on threefold axis.

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Received: 10 February 2018

Accepted: 14 April 2018

Published: 7 May 2018

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Selection and Peer-review under the responsibility of the RFYS Conference Committee.

1. Introduction

$\text{A}^{III}\text{BO}_3$ (where A – Fe, Al, In, Ti, Sc, V, Cr, Yb) metal orthoborates have been known for many years to be isostructural with calcium carbonate, CaCO_3 [1].

Particularly interesting is iron borate FeBO_3 , which is a weak antiferromagnet at ambient conditions. The combination of optical transparency in the visible spectral range with spontaneous magnetization at room temperature allows use of FeBO_3 in magneto-optical devices [2].

The functional characteristics of iron borate are dependent on 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_2O_3 and Fe_3BO_6 with norbergite structure [3].

Since, there are no data on the thermal expansion coefficients of iron borate FeBO_3 in the literature [4]. In this work we report the results of studying of FeBO_3 lattice parameters by high-temperature X-ray diffraction.

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2. Object and method of research

Iron borate crystallize in the calcite-type structure with space group $R\bar{3}c$. It is formally described as formed by slightly distorted $[\text{FeO}_6]$ octahedra whose O atoms belong to different $[\text{BO}_3]$ triangulars. $[\text{BO}_3]$ groups present reversed orientations alternating layers; while $[\text{FeO}_6]$ octahedral share corners with other six octahedral, three from the upper layer and three from the lower layer, Figure 1.

The space group has an R-type Bravais lattice; thus, the unit cell parameters can be specified in both primitive rhombohedral (table 1) and triple hexagonal systems.

The rhombohedral parameters of FeBO_3 structure: $a_r=5.52 \text{ \AA}$, $\alpha_r=49.54^\circ$, $V_r=89.532 \text{ \AA}^3$; the hexagonal parameters: $a_h=4.626(1) \text{ \AA}$, $c_h=14.496(6) \text{ \AA}$, $V_h=268.596 \text{ \AA}^3$, [3]. The rhombohedral FeBO_3 unit cell contain two formula units.

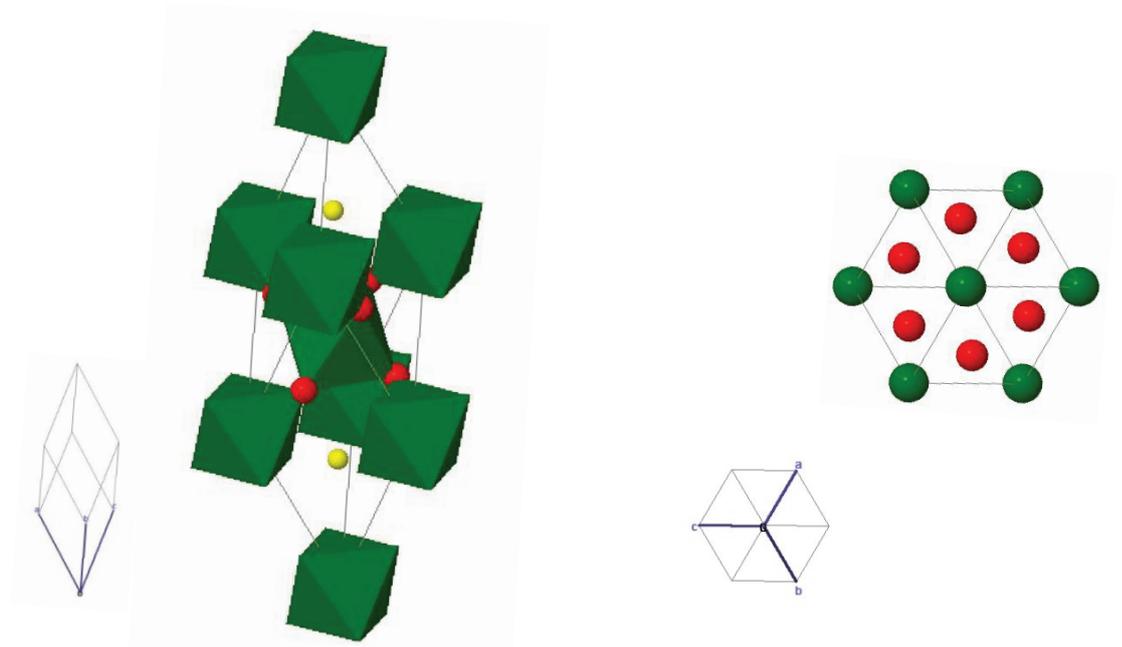


Figure 1: The primitive rhombohedral unit-cell of the FeBO_3 . An $[\text{FeO}_6]$ octahedron is represented in green. Fe, B and O atoms are represented in green, yellow and red spheres, respectively.

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 on SmartLab Rigaku diffractometer (CuK_α) in the temperature range from 25°C to 600°C . The XRD investigation of FeBO_3 was performed in the angle range $2\theta = 20^\circ - 100^\circ$ in steps $\Delta(2\theta) = 0.02^\circ$, Figure 2.

TABLE 1: Coordinates of the atoms in rhombohedral FeBO₃ unit-cell, where $x_r=0,5481$ [2].

Symmetry of the position	Atoms	Coordinates (relative units)
S_6	Fe	$0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2};$
D_3	B	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4};$
C_2	O	$\pm \left(x_r, \frac{1}{2} - x_r, \frac{1}{4}; \frac{1}{2} - x_r, \frac{1}{4}, x_r; \frac{1}{4}, x_r, \frac{1}{2} - x_r \right)$

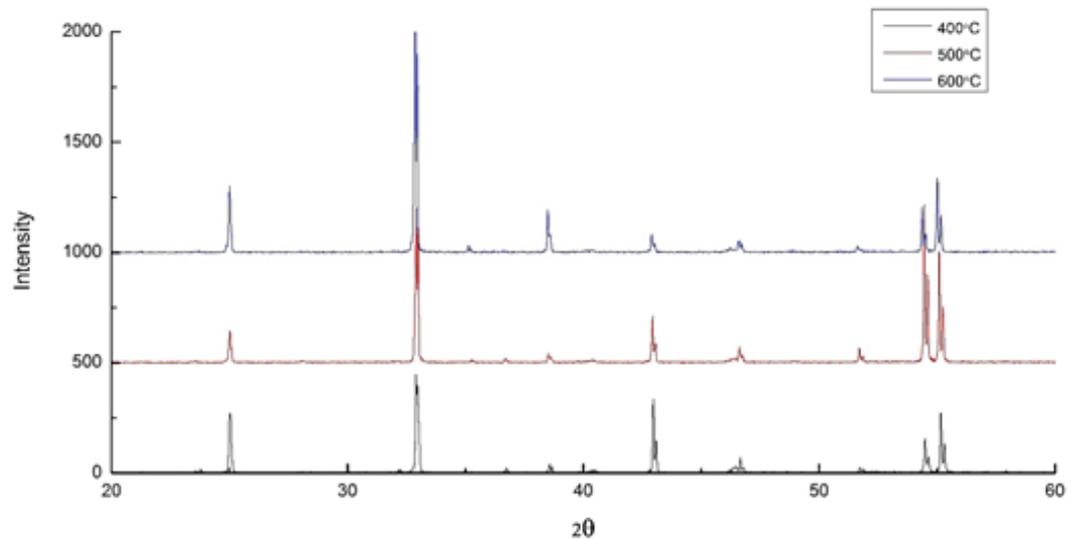


Figure 2: The X-ray powder diffraction patterns of FeBO₃ at 400°C, 500°C and 600 °C.

3. Analysis and discussion

The structure parameters of FeBO₃ were determined according to Bragg’s law, [5]:

$$n\lambda = 2d\sin\theta \tag{1}$$

where n - order of diffraction,

λ - X-ray wavelength, d - interplane distance,

θ - Bragg’s angle.

Indexing of diffractograms of FeBO₃ at the different temperatures was carried out, table 2.

The unite cell parameters of both systems calculated on the program [6] as a function of temperature are shown at table 3.

TABLE 2: Interference indexes of rhombohedral cell and structural characteristics d/n (Å) of $FeBO_3$ at room temperature and at 400°C, 500°C and 600°C.

(h k l)	d/n (25°C)	d/n (400°C)	d/n (500°C)	d/n (600°C)
(1 1 0)	3,507	3,559	3,556	3,558
(2 1 1)	2,688	2,720	2,719	2,723
(2 2 2)	2,415	2,444	2,447	2,552
(1 0 $\bar{1}$)	2,314	2,332	2,335	2,336
(2 1 0)	2,088	2,104	2,105	2,106
(2 0 0)	1,931	1,953	1,947	1,962
(2 2 0)	1,753	1,766	1,767	1,769
(3 2 1)	1,671	1,689	1,683	1,686
(3 3 2)	1,650	1,659	1,666	1,668

TABLE 3: Temperature dependence of lattice constants and cell volumes of rhombohedral (r) and hexagonal (h) systems of $FeBO_3$.

	25, °C	400, °C	500, °C	600, °C
$a_r, \text{Å}$	5,5194±0,0003	5,5662±0,0005	5,5750±0,0004	5,5793±0,0005
$\alpha_r, \text{Å}$	49,5806±0,001	49,5350±0,004	49,4570±0,001	49,4710±0,001
$V_r, \text{Å}^3$	89,598±0,017	91,766±0,038	91,971±0,018	92,227±0,020
$a_h, \text{Å}$	4,6285±0,0003	4,6620±0,0008	4,6642±0,0003	4,6691±0,0003
$c_h, \text{Å}$	14,4878±0,0011	14,6313±0,0011	14,6445±0,0011	14,6544±0,0014
$V_h, \text{Å}^3$	268,79±0,03	275,41±0,03	275,91±0,03	276,68±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:

$$a(t) = a_0 + a_1 \cdot t + a_2 \cdot t^2 \tag{2}$$

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 4.

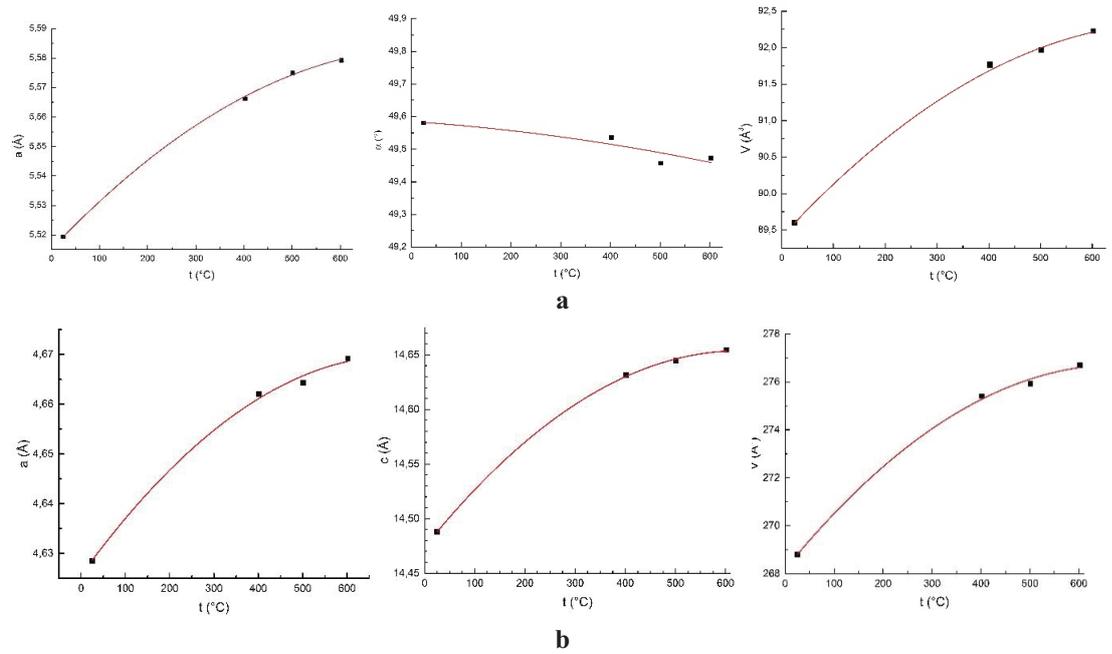


Figure 3: Temperature dependences of FeBO₃ structure parameters: (a) rhombohedral system, (b) hexagonal system. Experimental values are shown as points (error bars are smaller than the symbols used).

TABLE 4: Dependence of the lattice constants and volumes V of FeBO₃ on temperature.

Parameter	a_0	a_1	a_2
$a_r, \text{Å}$	5,5150	$1,7313 \cdot 10^{-4}$	$-1,0933 \cdot 10^{-7}$
$\alpha_r, ^\circ$	49,5942	$-5,5588 \cdot 10^{-4}$	$5,7349 \cdot 10^{-7}$
$V_r, \text{Å}^3$	89,410	0,0077	$-5,043 \cdot 10^{-6}$
$a_h, \text{Å}$	4,6255	$1,2290 \cdot 10^{-4}$	$-8,5442 \cdot 10^{-8}$
$c_h, \text{Å}$	14,4740	$5,6931 \cdot 10^{-4}$	$-4,4978 \cdot 10^{-7}$
$V_h, \text{Å}^3$	268,189	0,0250	$-1,835 \cdot 10^{-5}$

With respect to the definition of the coefficient of the thermal expansion, [5]:

$$a = \frac{1}{a_0} \cdot \frac{da}{dt}, \tag{3}$$

were da – difference of lattice parameters a for the interval dt ,

a_0 – the lattice parameters at 0°C,

dt – difference of temperature.

we obtain from (2) the dependence of thermal expansion coefficient on temperature:

$$a(t) = a_1 + a_2 \cdot t \tag{4}$$

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 5.

TABLE 5: Linear and volumetric thermal expansion parameters for FeBO₃.

Coefficients α, C^{-1}	a_1	a_2
$\alpha_{\perp z}$	$2,6571 \cdot 10^{-5}$	$-3,6943 \cdot 10^{-8}$
$\alpha_{\parallel z}$	$3,9333 \cdot 10^{-5}$	$-6,2151 \cdot 10^{-8}$
α_V	$9,3255 \cdot 10^{-5}$	$-1,3683 \cdot 10^{-7}$

Orientation dependence of the thermal expansion coefficients of the trigonal crystals described by equation [7]:

$$r = \alpha_r = \alpha_{\perp z} \sin^2 \theta + \alpha_{\parallel z} \cos^2 \theta \tag{5}$$

where r - radius-vector,

$\alpha_{\perp z}$ - CTE of perpendicular to main axis,

$\alpha_{\parallel z}$ - CTE of direction along to main axis.

θ - angle of the spherical coordinate system.

The three-dimensional thermal expansion diagrams of FeBO₃ drawing in MathCad are shown in Figure 4.

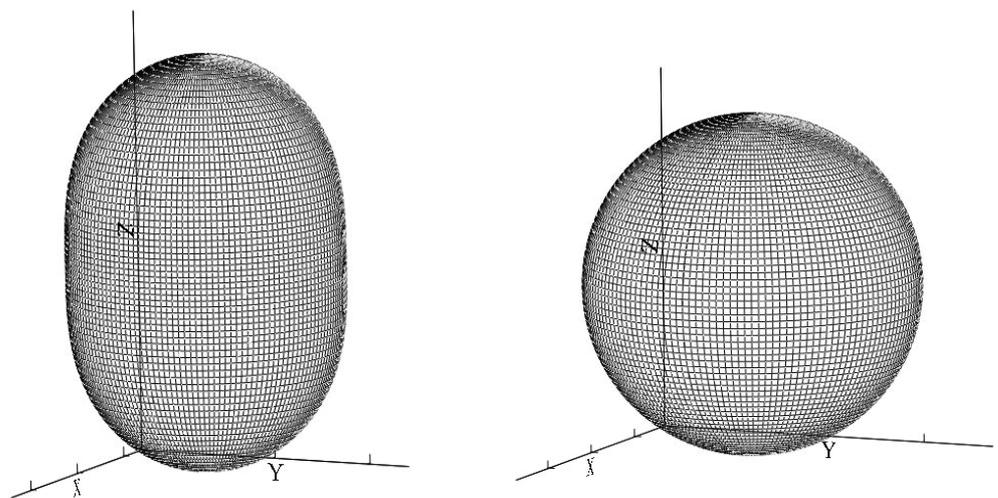


Figure 4: Indicatory surface of thermal expansion of FeBO₃: **a)** at room temperature ($\alpha_{\perp z} = 26,571 \cdot 10^{-6} C^{-1}$ and $\alpha_{\parallel z} = 39,33 \cdot 10^{-6} C^{-1}$); **b)** at 400 °C - 600 °C ($\alpha_{\perp z} = 8,0995 \cdot 10^{-6} C^{-1}$ and $\alpha_{\parallel z} = 8,2575 \cdot 10^{-6} C^{-1}$).

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. It can be seen that the thermal expansion of FeBO_3 is anisotropic, being greatest for the Z-axis (i.e. for the direction along the axis of the 3-order symmetry) and smallest for the direction perpendicular to the Z-axis.

In that below Neel point $T_N = 75^\circ\text{C}$, FeBO_3 is an easy plane weak ferromagnet with the anomalous temperature variation of the thermal expansion near the phase transition temperature [4], further studies are needed in this temperature range.

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