

**Volume 78 (2022)**

**Supporting information for article:**

**Crystal structure of bismuth-containing  $\text{NdFe}_3(\text{BO}_3)_4$  in the temperature range 20–500 K**

**Ekaterina S. Smirnova, Olga A. Alekseeva, Alexander P. Dudka, Igor A. Verin, Vladimir V. Artemov, Marianna V. Lyubutina, Irina A. Gudim, Kirill V. Frolov and Igor S. Lyubutin**

## S1. Analysis of temperature dependencies of lattice parameters

The temperature dependence of the unit cell parameters  $a$ ,  $b$ ,  $c$ , and volume  $V$  of neodymium iron borate  $(\text{Nd}_{0.91}\text{Bi}_{0.09})\text{Fe}_3(\text{BO}_3)_4$  was obtained in the range 20 – 293 K with a step of 5-10 K using a single-crystal HUBER-5042 diffractometer with a point detector, equipped with a closed-cycle helium cryostat DIPLEX DE-202 (Dudka *et al.*, 2017*a* and 2017*b*).

The temperature dependence of the unit cell parameters  $a$ ,  $b$ ,  $c$  and volume  $V$  of the  $(\text{Nd}_{0.91}\text{Bi}_{0.09})\text{Fe}_3(\text{BO}_3)_4$  crystal in the range 90 – 500 K was obtained using a CCD Xcalibur EOS S2 diffractometer (Rigaku Oxford Diffraction) with a Cobra Plus (Oxford Cryosystems) temperature attachment with open-flow nitrogen cooling.

To compare the structural data, temperature dependencies of  $a$ ,  $b$ ,  $c$ , and  $V$  of Nd-iron borate measured using the CCD Xcalibur diffractometer were normalized to the curves obtained using the reference diffractometer HUBER-5042 (Dudka *et al.*, 2016).

When calculating the parameters of the crystal lattice, the setting angles of few reflections (24-96) are measured using a diffractometer with a point detector (HUBER-5042, CAD-4f Enraf-Nonius). This technique has several advantages.

First, the position of the center of gravity of the reflection is determined after careful measurement of its profile with a small step (0.001-0.01 degrees, 48-96 points per line). When using a diffractometer with a CCD-detector, the scanning angle step is usually 0.3-1 degrees (0.5 degrees in this work), which introduces a noticeable error in the value of the calculated center of gravity of the reflection profile, especially in the presence of a  $K_\alpha$ -doublet in the radiation (Paciorek *et al.*, 1999).

Secondly, the list of reflections for refinement of the orientation matrix and unit cell parameters using a diffractometer with a point detector is balanced, which ensures compensation for many systematic errors of the diffractometer. The most important in this aspect is the use of sets of reflections, uniformly distributed in reciprocal space and measured at angles  $\theta$  that are identical in absolute value but different in sign. When a diffractometer with a two-dimensional CCD detector is used, the systematic errors are compensated by the large redundancy of measurements, but the measurement conditions are not sufficiently balanced, which results in incomplete compensation. In particular, due to time constraints, detector positions at negative angles  $\theta$  are rarely used.

It is of great importance also to consider the sample eccentricity (Hamilton, 1974), which is not compensated by the CCD Xcalibur EOS S2 diffractometer.

A consequence of the methodological imperfections of diffractometers with a two-dimensional CCD detector is that the calculated error of the unit cell parameters increases by up to 10 times (Dudka & Mill, 2014; Tyunina *et al.* 2010), and there is a systematic deviation of unit cell parameters from the parameters obtained using diffractometers with a point detector.

Therefore, the matching coefficient of the lattice parameters, obtained using the CAD4f Enraf Nonius (N) and CCD Xcalibur EOS S2 (X) diffractometers, was calculated in (Dudka *et al.* 2019b; Khrykina *et al.*, 2020):

$$k_1 = N/X = 1.000470828275271 \quad (1);$$

as well as CAD4f Enraf Nonius (N) and HUBER-5042 (H) diffractometers matching coefficient:

$$k_2 = N/H = 0.99998072 \quad (2).$$

Hence, the ratio of the lattice parameters for the HUBER-5042 (H) and CCD Xcalibur EOS S2 (X) diffractometers:

$$k_1/k_2 = H/X = (N/X) / (N/H) \quad (3);$$

$$X = H * k_2/k_1 = H * 0.99998072/1.000470828275271 = H * 0.9995101303 \quad (4).$$

Thus, the final coefficient for the transformation of the lattice parameters  $a$ ,  $b$ ,  $c$  is  $k = 0.9995101303$ .

Uncalibrated values of the unit cell parameters obtained at room temperature with a CCD Xcalibur EOS S2 diffractometer are  $a = 9.58150(10) \text{ \AA}$ ,  $c = 7.59700(10) \text{ \AA}$ ,  $V = 603.878(12) \text{ \AA}^3$ .

After transforming the parameters using the coefficient  $k = 0.9995101303$ , we have:

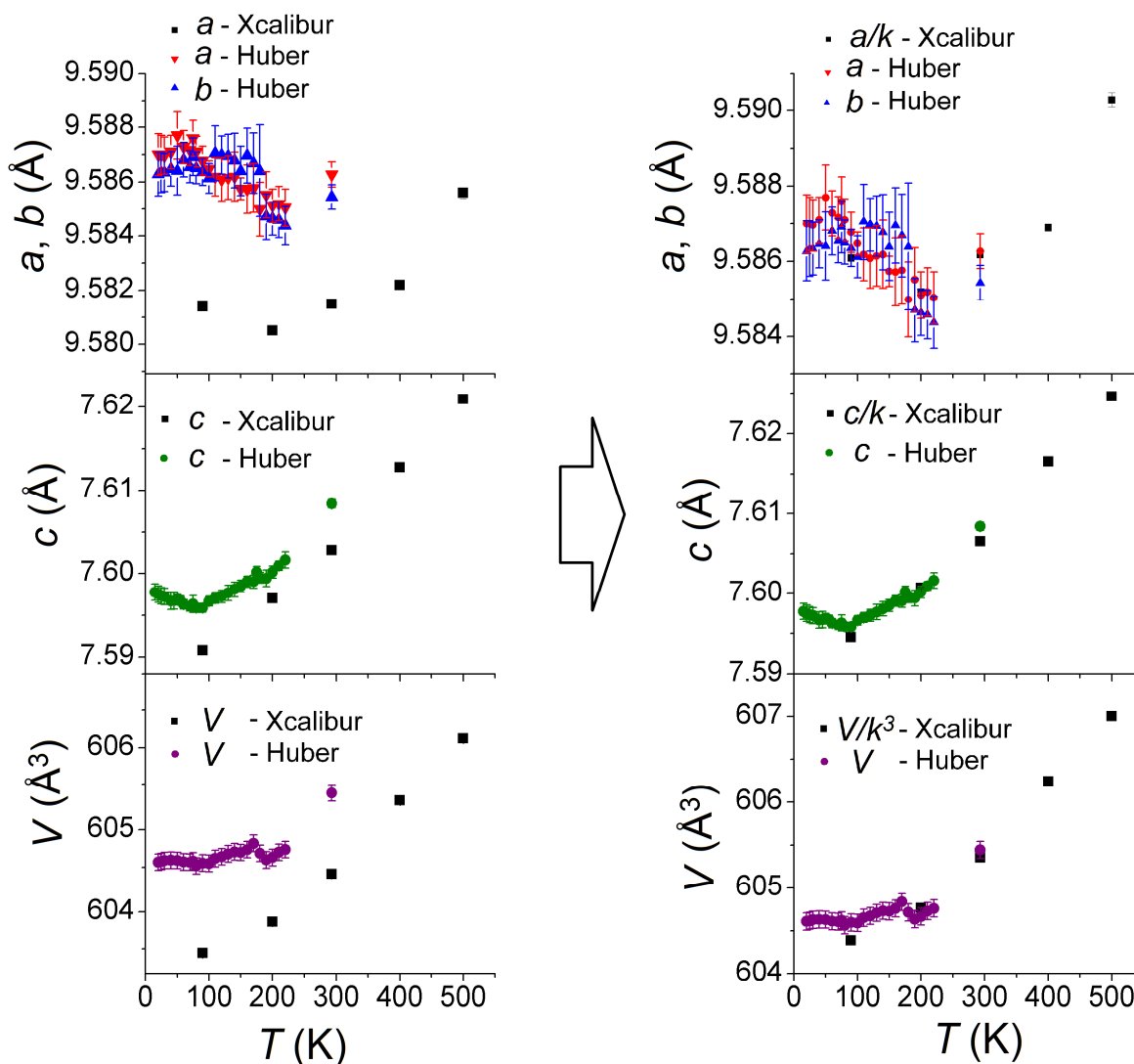
$$a_{\text{converted}} = 9.58150 / 0.9995101303 = 9.5862(1) \text{ \AA},$$

$$c_{\text{converted}} = 7.59700 / 0.9995101303 = 7.6007(1) \text{ \AA},$$

$$V_{\text{converted}} = 603.878 / 0.9995101303^3 = 604.174(12) \text{ \AA}^3.$$

Initial measured CCD Xcalibur values of  $a$ ,  $b$ ,  $c$  and  $V$  are shown in Fig. S1 (left). The values transformed using the matching coefficient are shown in Fig. S1 (right). It is easy to see, that the temperature curves measured using a CCD Xcalibur EOS S2 diffractometer fit well the curves obtained using a HUBER-5042 diffractometer.

It should be noted that the coefficient  $k = 0.9995101303$  was originally obtained when structural data for another family of compounds were brought in accordance (Dudka *et al.* 2019b; Khrykina *et al.* 2020). The good agreement of the  $k$ -transformed temperature curves for the lattice parameters of the  $(\text{Nd}_{0.91}\text{Bi}_{0.09})\text{Fe}_3(\text{BO}_3)_4$  crystal confirms that the reason for the discrepancy between the data is the instrumental model. The matching coefficients obtained for different diffractometers can be used to measure the lattice parameters of various compounds.



**Figure S1** Temperature dependence of parameters  $a$ ,  $b$ ,  $c$  and unit cell volume  $V$  of  $(\text{Nd}_{0.91}\text{Bi}_{0.09})\text{Fe}_3(\text{BO}_3)_4$  single crystal. The values obtained directly with CCD Xcalibur EOS S2 and HUBER-5042 diffractometers are on the left. The values obtained using a CCD Xcalibur EOS S2 diffractometer, brought in accordance with the temperature dependence obtained with the “reference” Huber diffractometer using the coefficient  $k = 0.9995101303$  are on the right.

## S2. Determination of characteristic temperatures and static displacements of cations using the *DebyeFit* program

The structural analysis allows one to determine the position of the scattering centers of atoms, as well as the atom deviations from equilibrium positions. Atomic displacements are defined as the density of the probability of atoms in a certain point in space. In the traditional method, their contribution to the structure factor is independent of temperature (Willis & Pryor, 1975). Temperature-dependent ADP models (Bürgi *et al.* 2000; Hoser *et al.* 2016) have not become as widespread as a probabilistic model, due to inaccurate describing experimental data. The reason for the insufficient accuracy of the models, which have more physical meaning than the probabilistic model, is that taking into account only the dynamic component is insufficient. The

physics of X-ray, neutron and electron scattering is such that the calculated ADPs include both thermal motion and static atomic disordering (Trueblood *et al.* 1996).

Recently, to describe the temperature dynamics of ADP, Dudka *et al.* (2019a) proposed extended Einstein and Debye models, which application yields agreement between model and experimental data at a precision level of 0.3–2%.

The atomic displacement parameters in the extended Debye and Einstein models are considered as a combination of quantum zero-point vibrations (temperature-independent), thermal vibrations, and static atomic displacements (temperature-independent). Hence, the experimental  $U_{eq}$  can be described by the model

$$u_{calc} = xu_E + (1-x)u_D + u_{static} \quad (4),$$

where  $xu_E$  and  $(1-x)u_D$  is a phonon contribution to the Einstein and Debye approximations;

$u_{static}$  is a static shift of an atom from its position in the structural model;

$x$  is a refined parameter that determines the degree of interaction of an atom with its surroundings in the crystal lattice.

The average vibration frequency of the selected atom and its characteristic Einstein temperature  $T_E$  can be obtained by substitute  $x = 1$ . This option is most suitable for loosely bound atoms:

$$u_E = \frac{h^2}{4\pi^2 k_B m_a T_E} \left( \frac{1}{2} + \frac{1}{\exp\left(\frac{T_E}{T}\right) - 1} \right) \quad (5).$$

The maximum vibration frequency of the selected atom and its characteristic Debye temperature  $T_D$  correspond to  $x = 0$ , which is most suitable for atoms strongly associated with the environment:

$$u_E = \frac{3h^2}{4\pi^2 k_B m_a T_D} \left( \frac{1}{4} + \left( \frac{T}{T_D} \right)^2 \int_0^{\frac{T_D}{T}} \frac{y}{\exp(y) - 1} dy \right) \quad (6).$$

The contribution of the Einstein or Debye models to atomic displacements consists of zero-point quantum oscillations  $u_{E0}$  or  $u_{D0}$ , and a temperature-dependent part  $u_E(T)$  или  $u_D(T)$ , which can be associated with the thermal motion of atoms.

Specifically,

$$u_E = u_{E0} + u_E(T) \quad (7)$$

and

$$u_D = u_{D0} + u_D(T) \quad (8).$$

An estimate of the zero-point vibrations of atoms  $u_{E0}$  or  $u_{D0}$  can be obtained by substitute  $T = 0$  in the Einstein or Debye formulas, respectively.

Atomic displacements, which do not originate from thermal vibrations (Dudka *et al.* 2019a):

$$u_{shift} = u_{E0} + u_{static} \quad (9)$$

or

$$u_{shift} = u_{D0} + u_{static} \quad (10).$$

The listed parameters are determined by minimizing the difference between experimental and model data:  $\Sigma (u_{calc} - u_{obs})^2 \rightarrow \min$ .

Good agreement between the model parameters of the displacement  $u_{calc}$  and the experimental equivalent parameters of the displacement  $U_{eq}$  can be obtained only when: (1) a special data collection procedure applied aimed at obtaining reproducible results; (2) correct determination of the crystal temperature during

measurements takes is ensured; (3) the static shift of atoms is accounted for, i.e. when using an extended model which includes the  $u_{\text{calc}}$  term.

### S3. Atomic coordinates and equivalent isotropic displacement parameters in the (Nd<sub>0.91</sub>Bi<sub>0.09</sub>)Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> structure at several temperatures

**Table S1** Atomic coordinates and equivalent isotropic displacement parameters in the (Nd<sub>0.91</sub>Bi<sub>0.09</sub>)Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> structure at 90 K.

	$x/a$	$y/b$	$z/c$	$U_{eq}, \text{\AA}^2$
Nd1 / Bi1 (3a)	0	0	0	0.003628(10)
Fe1 (9d)	0.217477(12)	0.333333	0.333333	0.00302(2)
O1 (9e)	0.14420(6)	0.14420(6)	0.5	0.00430(9)
O2 (9e)	0.40981(7)	0.40981(7)	0.5	0.00574(11)
O3 (18f)	0.02648(5)	0.21492(6)	0.18474(7)	0.00499(8)
B1 (3b)	0	0	0.5	0.00390(19)
B2 (9e)	0.55382(9)	0.55382(9)	0.5	0.00434(16)

**Table S2** Atomic coordinates and equivalent isotropic displacement parameters in the (Nd<sub>0.91</sub>Bi<sub>0.09</sub>)Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> structure at 293 K.

	$x/a$	$y/b$	$z/c$	$U_{eq}, \text{\AA}^2$
Nd1 / Bi1 (3a)	0	0	0	0.007899(16)
Fe1 (9d)	0.217434(13)	0.333333	0.333333	0.00530(2)
O1 (9e)	0.14411(6)	0.14411(6)	0.5	0.00679(11)
O2 (9e)	0.41011(8)	0.41011(8)	0.5	0.01057(15)
O3 (18f)	0.02649(6)	0.21516(7)	0.18501(8)	0.00836(11)
B1 (3b)	0	0	0.5	0.0055(2)
B2 (9e)	0.55389(9)	0.55389(9)	0.5	0.00638(19)

**Table S3** Atomic coordinates and equivalent isotropic displacement parameters in the (Nd<sub>0.91</sub>Bi<sub>0.09</sub>)Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> structure at 500 K.

	$x/a$	$y/b$	$z/c$	$U_{eq}, \text{\AA}^2$
Nd1 / Bi1 (3a)	0	0	0	0.01219(3)
Fe1 (9d)	0.21730(2)	0.333333	0.333333	0.00786(4)
O1 (9e)	0.14399(9)	0.14399(9)	0.5	0.0098(2)
O2 (9e)	0.41041(11)	0.41041(11)	0.5	0.0153(3)
O3 (18f)	0.02643(9)	0.21507(10)	0.18507(12)	0.0123(2)
B1 (3b)	0	0	0.5	0.0077(4)
B2 (9e)	0.55400(13)	0.55400(13)	0.5	0.0088(3)

## References

- Bürgi, H. B. & Capelli, S. C. (2000). *Acta Cryst.* A56, 403–412.
- Dudka, A. P. & Mill', B. V. (2014) *Crystallogr. Rep.* **59**, 689–698.
- Hamilton W.C. International Tables for X-Ray Crystallography. 1974, Vol. 4, p. 273. Birmingham: Kynoch Press.
- Hoser, A. A. & Madsen, A. O. (2016). *Acta Cryst.* A**72**, 206–214.
- Trueblood, K. N., Bürgi, H.-B., Burzlaff, H., Dunitz, J. D., Gramaccioni, C. M., Schulz, H. H., Shmueli, U. & Abrahams, S. C. (1996). *Acta Cryst.* A**52**, 770–781.
- Tyunina, E. A., Kaurova, I. A., Kuz'micheva, G. M., Rybakov, V. B., Cousson, A. & Zaharko, O. (2010). *Fine Chemical Technologies.* **5**(1), 57-68. (In Russ.).
- Paciorek, W. A., Meyer, M. & Chapuis, G. (1999). *J. Appl. Cryst.* **32**, 11–14.
- Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge University Press.