

## X-ray Rietveld structure refinement and bond-valence analysis of chromium(III) orthoborate CrBO<sub>3</sub>

Anastasiya SERGEEVA<sup>1</sup>, Vasyl SIDEY<sup>2\*</sup>

<sup>1</sup> General and Inorganic Chemistry Department, Voronezh State University,  
Universitetskaya Pl. 1, 394006 Voronezh, Russian Federation

<sup>2</sup> Research Institute for Physics and Chemistry of Solids, Uzhgorod National University,  
Pidgirma St. 46, 88000 Uzhgorod, Ukraine

\* Corresponding author. Tel./fax: +38 03122 3 23 39; e-mail: vasylsidey@hotmail.com

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The crystal structure of chromium(III) orthoborate, CrBO<sub>3</sub>, has been refined using the Rietveld analysis of X-ray powder diffraction data. The refinement procedure was stopped when the intensity residual  $R_B = 3.58\%$  had been reached. CrBO<sub>3</sub> crystallizes in the rhombohedral structure type of calcite, space group *R-3c* (No. 167), with the lattice parameters (in hexagonal axes)  $a = 4.5754(4) \text{ \AA}$ ,  $c = 14.2514(15) \text{ \AA}$ ;  $Z = 6$ ;  $D_x = 4.273(1) \text{ g/cm}^3$ . The bond-valence analysis of the crystal structure of CrBO<sub>3</sub> confirmed the reliability of the structural model obtained.

Oxide materials / Chemical synthesis / Crystal structure / X-ray diffraction

### Introduction

For the first time, chromium(III) orthoborate, CrBO<sub>3</sub>, was synthesized by Tombs *et al.* [1] in 1963. By analyzing the X-ray powder diffraction pattern obtained for CrBO<sub>3</sub>, Tombs and co-workers concluded that this compound crystallizes in the rhombohedral structure type of calcite CaCO<sub>3</sub> [2]. However, in spite of the fact that CrBO<sub>3</sub> has been known for a long time as an antiferromagnetic material [3,4], the crystal structure of this compound has never been refined. Indeed, the present version of the Inorganic Crystal Structure Database [5] (last checked in February, 2013) contains only one entry for CrBO<sub>3</sub> (ICSD 43311) with the presupposed crystal structure of the title compound; but the article by Schmid [6] used as reference for that entry actually presents only the “*d*-spacings vs. intensity” powder diffraction data for CrBO<sub>3</sub>.

It should be noted that symmetrically regular boron(III) – oxygen coordination triangles (as in the calcite-type  $M^{III}BO_3$  orthoborate structures) are rather rare to occur in solids. So, being interested in the crystal chemistry of oxoborates, and exploring the “bond order (bond valence) vs. bond length” correlation curve for boron(III) – oxygen chemical bonds [7,8], we decided to refine the crystal structure of chromium(III) orthoborate CrBO<sub>3</sub> (containing the regular coordination triangle [BO<sub>3</sub>]) by using the

Rietveld method [9,10]. The main aim of the present work is to report the structure of CrBO<sub>3</sub> obtained by us from the Rietveld refinement.

### Experimental

The reactants used in the chemical synthesis were of a purity of 99.5 wt.% or better. Chromium(III) orthoborate, CrBO<sub>3</sub>, was synthesized by reaction between Cr<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> in molten B<sub>2</sub>O<sub>3</sub>, in essential accordance with the procedure developed and reported by Öztürk *et al.* [4] as “Experiment 6”. Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·15H<sub>2</sub>O and H<sub>3</sub>BO<sub>3</sub> were mixed in Cr : B = 1 : 4 ratio and manually ground in an agate mortar for half an hour. The resulting mixture was loaded into an alundum crucible and heated for 12 h at 1050°C. To remove excess B<sub>2</sub>O<sub>3</sub> in the product, the sample was washed with hot distilled water and then dried under vacuum.

Polycrystalline CrBO<sub>3</sub> was reground to a fine powder in an agate mortar and then investigated using the X-ray powder diffraction technique (XRD). Preliminary XRD experiments showed that the sample obtained in the above synthesis contained no impurities in detectable quantities; so a Rietveld refinement [9,10] of the crystal structure of CrBO<sub>3</sub> was attempted.

X-ray powder diffraction data used for the Rietveld refinement of the structure of  $\text{CrBO}_3$  were collected with a conventional Bragg-Brentano diffractometer DRON-3M in the step scan mode (Cu  $K\alpha$  radiation [11],  $20 \leq 2\theta \leq 100^\circ$ , step size  $0.02^\circ$ , counting time 10 s per step, room temperature).

The Rietveld refinement [9,10] procedures were performed using the program DBWS-9807a [12], an upgraded version of the classical program by Wiles and Young [13,14]. The Pearson VII [15] function was used for the simulation of the peak shape. Intensities within 32 times of the full-width-at-half-maximum (FWHM) were considered to contribute to the reflection. The background curve was modeled using the refinable fifth-order polynomial. Peaks below  $60^\circ$  ( $2\theta$ ) were corrected for asymmetry effects by using the Riello-Canton-Fagherazzi model [16]. Application of corrections for preferred orientation and surface roughness highly destabilized the least-squares refinement and did not improve the structural model of  $\text{CrBO}_3$ ; so these corrections were excluded from the final cycles of the Rietveld refinement.

The refinement converged with the profile residuals  $R_p = 6.50\%$  and  $R_{wp} = 7.70\%$ , and with the intensity residual  $R_B = 3.58\%$ . It should be noted that the above profile residuals are critically dependent on the background level, and low values of  $R_p$  and  $R_{wp}$  can actually indicate a high background level rather than the real profile agreement [17]. However, the  $R_B$  intensity residual (so-called “Bragg  $R$ -factor”) is not affected by the background level [17]; therefore, the fairly low  $R_B$  value obtained in the present work indicates reasonable agreement between the experimental and theoretical structural models of  $\text{CrBO}_3$ .

The measured density  $D_m$  of the compound  $\text{CrBO}_3$  was determined by pycnometry measurements, using toluene as the working liquid.

Experimental details and crystallographic data for the compound  $\text{CrBO}_3$  are collected in Table 1. Positional and isotropic displacement (“thermal”) parameters of the crystal structure of the title compound are given in Table 2; selected interatomic distances in the first coordination shells of the structure of  $\text{CrBO}_3$  are given in Table 3. Fig. 1 shows the final Rietveld plot for  $\text{CrBO}_3$ .

The compound  $\text{CrBO}_3$  crystallizes in the well-known rhombohedral structure type of calcite,  $\text{CaCO}_3$  [2]. The crystal structure of the title compound could be described as the framework formed by the  $[\text{CrO}_6]$  coordination octahedra and the  $[\text{BO}_3]$  coordination triangles. Every O atom in the structure of  $\text{CrBO}_3$  is shared by two  $[\text{CrO}_6]$  coordination octahedra and one  $[\text{BO}_3]$  coordination triangle. Fig. 2 illustrates the connectivity of the coordination shells  $[\text{CrO}_6]$  and  $[\text{BO}_3]$  in the crystal structure of  $\text{CrBO}_3$ .

More detailed information about the calcite structure type can be found, for example, in the classical book by A.F. Wells [18] or in any modern

textbook on inorganic crystal chemistry and mineralogy.

### Bond-valence analysis of the crystal structure of $\text{CrBO}_3$

Since the Rietveld method cannot, in general, compete with the single-crystal techniques in the reliability of crystal structure refinements [10], the structures obtained in the Rietveld refinement procedures should always be carefully tested for possible systematic errors. In order to check the reliability of the structural model obtained in the present work for the title compound, we employed the bond-valence analysis procedure [19,20].

The bond-valence model (BVM) in its modern form is a powerful and convenient tool for validating newly determined crystal structures and for predicting bond lengths in the structures of known chemical composition and presupposed bond-network topology [19,20]. Bond valence (BV)  $s$  is defined as a part of the “classical” atomic valence shared with each bond. According to the bond-valence sum (BVS) rule, the oxidation state (atomic valence)  $V_A$  of the central ion (atom) of the  $[\text{AX}_n]$  coordination shell can be calculated from the sum of the individual bond valences  $s_{AX}$ , as given in equation (1).

$$V_A = \sum_n s_{AX} \quad (1)$$

The valence of a bond (measured in “valence units”, v.u.) is considered to be a unique function of the bond length; and the most commonly adopted empirical expressions for the relationship between the bond valences  $s_{AX}$  and the bond lengths  $r_{AX}$  are equations (2) and (3), where  $r_0$ ,  $n$  and  $b$  are empirically determined parameters (BV parameters) for a given ion (atom) pair,  $r_0$  being the length of the conceptual bond of unit valence with  $s_{AX} = 1$  [21-24].

The  $b$  parameter in equation (3) is commonly taken to be the “universal constant” equal to  $0.37 \text{ \AA}$ , and the  $r_0$  parameters have been determined for ~1000 ion pairs, assuming  $b = 0.37 \text{ \AA}$  [23,24].

$$s_{AX} = [r_0 / r_{AX}]^n \quad (2)$$

$$s_{AX} = \exp[(r_0 - r_{AX})/b] \quad (3)$$

In well-determined, stable, ordered crystal structures, the BVS values calculated for all crystallographically distinct atoms from reliable BV parameters are typically very close to the expected  $V_A$  values; therefore, large deviations between the BVS and  $V_A$  values can be a symptom of the incorrectness of the structural model. A very useful measure for the failure of the BVS rule is the so-called “global instability index”  $G$  [19,20] defined by equation (4). Correctly determined, stable, ordered structures

**Table 1** Experimental details and crystallographic data for CrBO<sub>3</sub>.

Crystal system; space group	trigonal; <i>R</i> -3 <i>c</i> (No. 167)
Lattice parameters (hexagonal axes)	<i>a</i> = 4.5754(4) Å; <i>c</i> = 14.2514(15) Å
Cell volume	<i>V</i> = 258.37(6) Å <sup>3</sup>
Chemical formula weight	FW = 110.81
Formula units per cell	<i>Z</i> = 6
Calculated density	<i>D</i> <sub>x</sub> = 4.273(1) g/cm <sup>3</sup>
Measured density	<i>D</i> <sub>m</sub> = 4.23(2) g/cm <sup>3</sup>
Temperature of data collection	<i>T</i> = 293(2) K
Radiation type; wavelength	Cu <i>K</i> α; λ = 1.5419 Å
Powder diffractometer; geometry	DRON-3M; Bragg-Brentano
2θ scan range; step	20÷100°; 0.02°
Scan speed	10 s/step
Refinement program	DBWS-9807a
Peak shape function	Pearson VII
Peak asymmetry function	Riello-Canton-Fagherazzi
Background model	5 <sup>th</sup> order polynomial
Number of atom sites	3
Number of free structural parameters	6
Total number of free parameters	20
Profile <i>R</i> -factors	<i>R</i> <sub>p</sub> = 6.50%; <i>R</i> <sub>wp</sub> = 7.70%
Bragg <i>R</i> -factor	<i>R</i> <sub>B</sub> = 3.58%
Goodness of fit	<i>S</i> = 1.62

**Table 2** Atomic coordinates and isotropic displacement parameters for the crystal structure of CrBO<sub>3</sub>.

Site	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> [Å <sup>2</sup> ]
Cr	6 <i>b</i>	0	0	0	0.4(1)
B	6 <i>a</i>	0	0	¼	0.6(3)
O	18 <i>e</i>	0.3010(7)	0	¼	0.7(2)

**Table 3** Selected interatomic distances in the coordination shells of the structure of CrBO<sub>3</sub>.

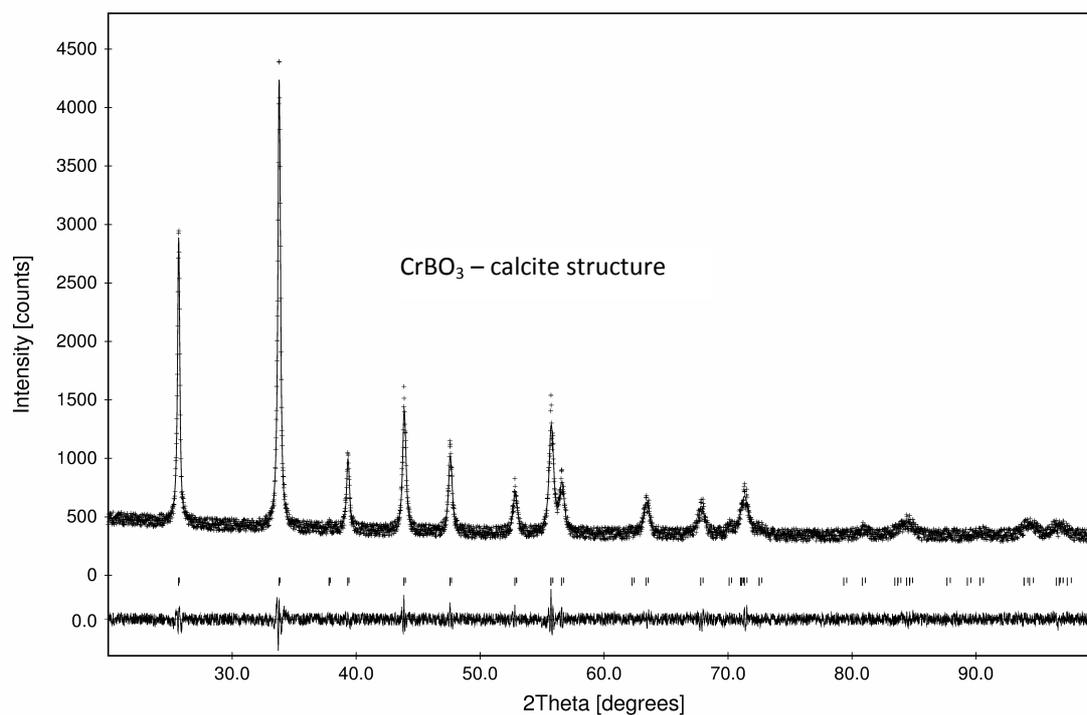
Coordination shell	Bond	Distance [Å]
[CrO <sub>6</sub> ]	Cr – O (×6)	1.996(2)
[BO <sub>3</sub> ]	B – O (×3)	1.377(3)
[OBCr <sub>2</sub> ]	O – Cr (×2)	1.996(2)
	O – B (×1)	1.377(3)

are rarely found with *G* greater than 0.2 v.u. [19,20]; and larger *G* values can usually be attributed to systematic errors in the crystal structure determinations and/or to the use of poorly determined BV parameters.

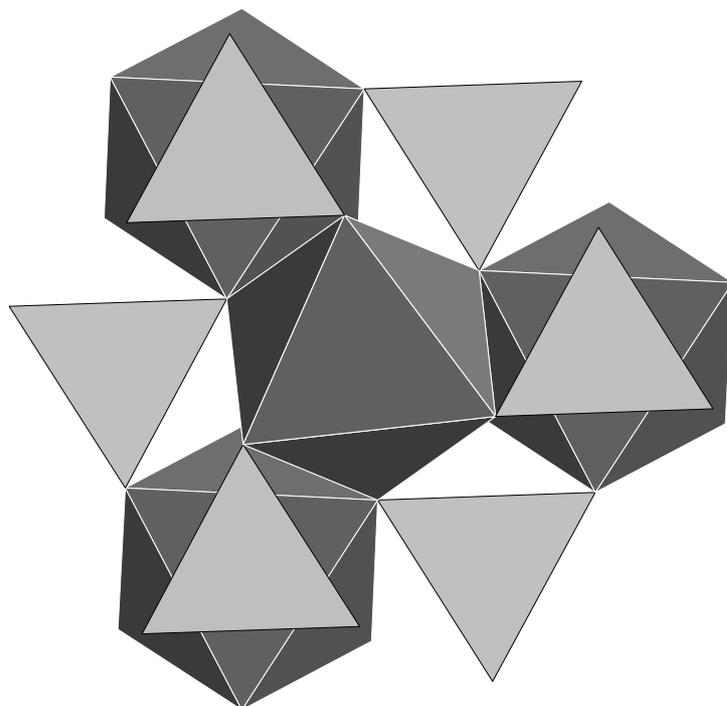
$$G = \langle (\text{BVS} - V_A)^2 \rangle^{0.5} \quad (4)$$

BV parameters relevant to the B<sup>3+</sup>/O<sup>2-</sup> and Cr<sup>3+</sup>/O<sup>2-</sup> ion pairs are quoted in the well-known collections of BV parameters by Brown and Wu [22] and Brese and O'Keeffe [24]. Brown and Wu [22] give *r*<sub>0</sub> = 1.378 Å

and *n* = 4.065 for the B<sup>3+</sup>/O<sup>2-</sup> ion pair (these BV parameters were taken from an earlier article by Brown and Shannon [21]), and *r*<sub>0</sub> = 1.733 Å and *n* = 5.2 for the Cr<sup>3+</sup>/O<sup>2-</sup> ion pair. Brese and O'Keeffe [24] in their tables of BV parameters give *r*<sub>0</sub> = 1.371 Å and *b* = 0.37 Å for the B<sup>3+</sup>/O<sup>2-</sup> ion pair, and *r*<sub>0</sub> = 1.724 Å and *b* = 0.37 Å for the Cr<sup>3+</sup>/O<sup>2-</sup> ion pair (both these sets of BV parameters were taken from an earlier work by Brown and Altermatt [23]). Fig. 3 illustrates the “bond order (bond valence) *s*<sub>AX</sub> vs. bond length *r*<sub>AX</sub>” correlation curves defined by the Brown-Wu [22] and Brese-O'Keeffe [24] parameters



**Fig. 1** Experimental (crosses), theoretical (solid line), and difference (solid line at the bottom) powder XRD patterns for CrBO<sub>3</sub>; reflection positions are marked by vertical bars.



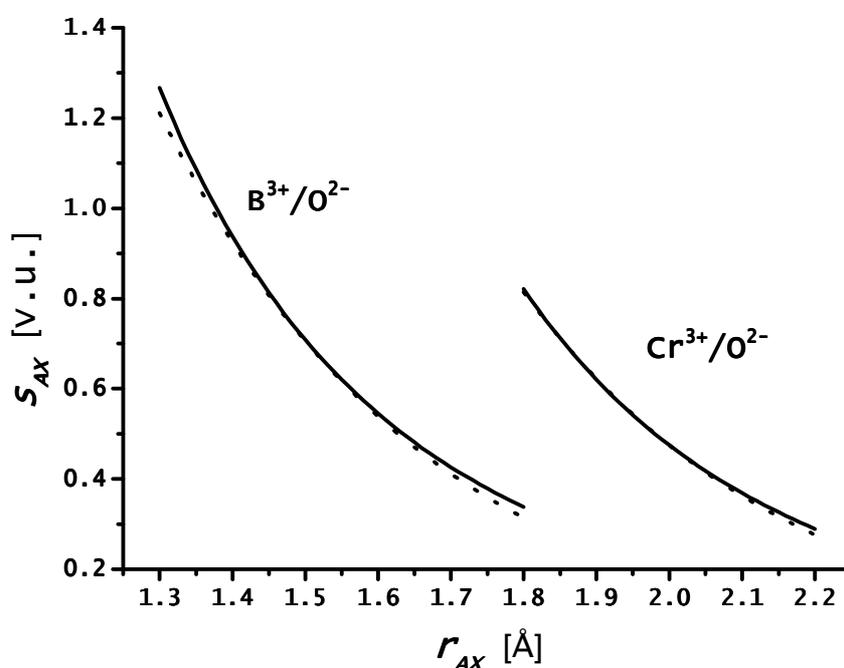
**Fig. 2** Fragment of the crystal structure of CrBO<sub>3</sub>: connectivity of the [BO<sub>3</sub>] coordination triangles and [CrO<sub>6</sub>] coordination octahedra.

for the  $B^{3+}/O^{2-}$  and  $Cr^{3+}/O^{2-}$  ion pairs. One can see that, in spite of the methodologically different and *independent* procedures used for determining the  $(r_0; n)$  and  $(r_0; b)$  sets of BV parameters [21-24], the curves defined for the same ion pair are very close to each other over the range of typical interatomic distances. Taking this fact into account, the fair reliability of the Brown-Wu [22] and Brese-O'Keeffe [24] parameters reported for the  $B^{3+}/O^{2-}$  and  $Cr^{3+}/O^{2-}$  ion pairs has been confirmed, and the  $G$  values calculated from the above parameters were considered as an adequate measure for the correctness of the structural model obtained in the present work. As clearly demonstrated in an earlier work by one of the authors (V.S.) [25], a large  $G$  value can be an *artifact* of poorly determined BV parameters; in this case, a

methodologically correct BV analysis of the structure at hand requires some additional efforts to calculate improved BV parameters.

The results of the BV analysis of the structure of the title compound are given in Table 4. As seen, the BVS values calculated for the individual atoms in the structure of  $CrBO_3$  are reasonably close to the expected  $V_A$  values, and the  $G$  values calculated for the whole structure are much less than 0.2 v.u.

Taking into account the fairly low  $R_B$  value (Table 1), the quite smooth difference plot (Fig. 1) and the low  $G$  values obtained in the present work for the crystal structure of  $CrBO_3$ , one may conclude that the structural model reported here for the title compound has been determined with no serious errors.



**Fig. 3** “Bond order (bond valence)  $s_{AX}$  vs. bond length  $r_{AX}$ ” correlation curves defined by the Brown-Wu [22] (solid lines) and Brese-O'Keeffe [24] (dotted lines) parameters for the  $B^{3+}/O^{2-}$  and  $Cr^{3+}/O^{2-}$  ion pairs.

**Table 4** Bond-valence analysis of the crystal structure of  $CrBO_3$ .

Atom	Coordination shell	Bond-valence sum (BVS) [v.u.] <sup>a</sup>	
		(i)	(ii)
$Cr^{3+}$	$[CrO_6]$	2.878 (−4%)	2.877 (−4%)
$B^{3+}$	$[BO_3]$	3.009 (+0%)	2.952 (−2%)
$O^{2-}$	$[OBrCr_2]$	1.962 (−2%)	1.943 (−3%)
		$G = 0.07$ v.u.	$G = 0.08$ v.u.

<sup>a</sup>The BVS and  $G$  values were calculated using the BV parameters reported for the  $B^{3+}/O^{2-}$  and  $Cr^{3+}/O^{2-}$  ion pairs by (i) Brown and Wu [22] and (ii) Brese and O'Keeffe [24] (see the text).

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