Structure of the fully ferroelectric/fully ferroelastic orthorhombic room-temperature phase of cobalt bromine boracite, $Co_3B_7O_{13}Br$ and nickel chlorine boracite, $Ni_3B_7O_{13}Cl$

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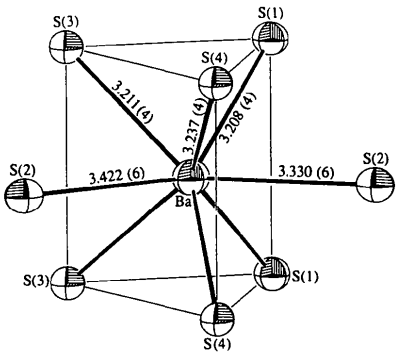

Fig. 3. An *ORTEP* drawing of the BaS_8 polyhedron shown in a bicapped trigonal prismatic configuration. The anisotropic atoms are presented at 90% probability. The Ba—S bond lengths are given in ångströms.

chiometry. Otherwise the t.p. Ba—S distances are in the range 3.21–3.24 Å, which is consistent with the crystal radii sum, 3.26 Å, of eight-coordinated Ba^{2+} (1.56 Å) and six-coordinated S^{2-} 1.70 Å, according to Shannon.

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Structure of the Fully Ferroelectric/Fully Ferroelastic Orthorhombic Room-Temperature Phase of Cobalt Bromine Boracite, $Co_3B_7O_{13}Br$ and Nickel Chlorine Boracite, $Ni_3B_7O_{13}Cl$

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Abstract. The X-ray crystal structures of optically controlled single-domain crystals of fully ferroelectric/fully ferroelastic cobalt bromine boracite, $Co_3B_7O_{13}Br$ (Co–Br) at 298 K [$M_r = 540.38$, orthorhombic, $Pca2_1$, $a = 8.5614$ (2), $b = 8.5657$ (2), $c = 12.1196$ (3) Å, $V = 888.78$ (4) Å^3, $Z = 4$, $D_x = 4.04$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 10.61$ mm^{-1}, $F(000) = 1020$, $R = 7.0$, $wR = 5.4\%$, 2824 reflections] and of nickel chlorine boracite, $Ni_3B_7O_{13}Cl$ (Ni–Cl) at 298 K [$M_r = 495.25$, orthorhombic, $Pca2_1$, $a = 8.5105$ (4), $b = 8.4984$ (4), $c = 12.0324$ (5) Å, $V = 870.25$ (7) Å^3, $Z = 4$, $D_x = 3.78$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 6.8$ mm^{-1}, $F(000) = 960$, $R = 3.5$, $wR = 3.1\%$, 2082 reflections] are reported. The metal surroundings of Co–Br and Ni–Cl were analyzed in detail and show two metal sites (Co2, Co3; Ni2, Ni3) with chemically similar environments and one metal site (Co1; Ni1) with a different environment. Six B atoms have a tetrahedral or slightly distorted tetrahedral coordination, whereas one B atom (B4) has triangular surroundings in both compounds.

Introduction. Cobalt bromine boracite and nickel chlorine boracite undergo respective improper phase transitions at 466 and 608 K from a cubic

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paramagnetic/paraelectric high-temperature phase ($F\bar{4}3c$) to an orthorhombic paramagnetic/ferroelectric low-temperature phase ($Pca2_1$). Both Co–Br and Ni–Cl undergo a second-order phase transition to a weakly ferromagnetic phase at 17.5 and 9 K, respectively, with an associated magnetic point-group symmetry change $mm21' \rightarrow m'm2'$ [Tolédano, Schmid, Clin & Rivera, 1985; Clin, Rivera & Schmid, 1988 (Co–Br); Rivera & Schmid, 1991 (Ni–Cl)]. With a view to neutron-diffraction studies of the ferromagnetic/ferroelectric low-temperature phases accurate X-ray structural data were required.

Experimental. Crystals of Co–Br were prepared by chemical transport reactions (Schmid, 1965). Several refinements of small, as-grown crystals, which appeared to be optically single domain, failed. The crystal used in this study was prepared from a polished $(100)_{cub}$ plate by mechanical compression and subsequent abrasion of the remaining domains. A highly twinned, 0.0065 cm thick $(100)_{cub}$ plate of cobalt bromine boracite was compressed along a [110] direction by means of a pair of tweezers, using a polarizing light microscope for simultaneous control of the domain state. The movement of the domain walls could be observed and guided *in situ* along different directions. Subsequent compression of different parts of the crystal-plate corners allowed an increase in size of some monodomain parts in the plate. The single-domain crystal to be studied was then broken out by means of a steel needle; finally, residual 90° domains near the corners were polished off. Crystal dimensions were approximately 0.02 $\times$ 0.044 $\times$ 0.0065 cm. Lattice parameters were determined on an automatic diffractometer by measuring 25 reflections between $2\theta_{min} = 50.5$ and $2\theta_{max} = 52.0°$. Space group $Pca2_1$ was confirmed through absent reflections. 14 493 reflections were collected on a Nonius CAD-4 diffractometer (θ–2θ scan mode) up to $[(\sin\theta)/\lambda]_{max} = 0.81$ Å^{-1} ($-12 \le h \le 12$, $-12 \le k \le 12$, $-17 \le l \le 17$). Two standard reflections (004 and 404) were measured every hour; they varied by less than 4%. Intensities were corrected for these variations. Absorption was corrected by Gaussian absorption correction; maximal and minimal values were found to be 8.95 and 1.98 respectively. The internal confidence value was 3.5% for 3732 independent reflections. 2864 unique reflections had $I > 3\sigma(I)$.

Single crystals of Ni–Cl were also grown by chemical transport reaction (Schmid, 1965; Schmid & Tippmann, 1979). The monodomain crystal to be studied was cut out of a nearly monodomain $(100)_{cub}$ plate, polished from a suitable crystal. Sample dimensions were 0.0048 $\times$ 0.016 $\times$ 0.032 cm. Lattice parameters were determined from 27 reflections measured on a Philips diffractometer between $2\theta_{min} = 50.0$ and $2\theta_{max} = 68.0°$ (θ–2θ scan mode). Atomic scattering factors and f', f'' values were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Space group $Pca2_1$ was confirmed through absent reflections. 3050 reflections were measured up to $[(\sin\theta)/\lambda]_{max} = 0.70$ Å^{-1} ($-11 \le h \le 11$, $-11 \le k \le 11$, $-16 \le l \le 16$). Two standard reflections ($\bar{2}\bar{2}4$ and $\bar{2}02$) measured every hour varied by less than 3%. Intensities were corrected for these variations. Absorption was corrected by Gaussian absorption correction; maximal and minimal values were found to be 2.18 and 1.39, respectively. The internal confidence value was 1.0% for 2846 independent reflections. 2099 unique reflections had $I > 3\sigma(I)$.

Starting values for the refinements were taken from the work of Abrahams, Bernstein & Svenson (1981) but had to be adapted to the new definition of the space group by shifting the origin by $\frac{1}{4}, \frac{1}{4}, z$. Refinements (based on F) were performed with the program *XTAL* (Hall & Stewart, 1990) by minimizing the function $\sum w_i(|F_r|_i - |F_c|_i/k_i)^2$ with $w_i = 1/\sigma^2(F_r)_i$. The absolute sense of the polar axis was determined by refinement of the absolute structure factor (Flack, 1983; Bernardinelli & Flack, 1985). Atomic positions for both structures are listed together with temperature factors in Table 1. They were partially standardized (Gelato & Parthé, 1987). For Co–Br and Ni–Cl 118 parameters each (one scale factor, one absolute structure factor, one extinction factor, 71 positional parameters and 44 temperature factors) were refined. In the final stage 60 reflections at low angle were rejected for Co–Br owing to strong extinction (Thornley & Nelmes, 1974). The final confidence values were $R = 7.0$, $wR = 5.4\%$, $S = 5.4$ for 2822 reflections for Co–Br, and $R = 3.5$, $wR = 3.1\%$, $S = 3.9$ for 2082 reflections for Ni–Cl. Inclusion of all reflections (2864) for Co–Br gave confidence factors of $R = 7.5$, $wR = 7.2\%$.* Maximum Δ/σ for Co–Br was 0.017 and for Ni–Cl was 0.0001. Maximal residues were 5.3 and 1.4 e Å^{-3} for Co–Br and Ni–Cl, respectively.

Discussion. Table 2 shows that both for Ni–Cl and Co–Br, as well as for other orthorhombic boracites, the c axis is always longer than the other two pseudocubic $[100]_{cub}$ directions given by $[(a + b)/2]\sqrt{2}$. This means that squeezing along $[100]_{cub}$ may lead, in the worst case, to a crystal with four domains, all having their c axes perpendicular to the squeezing direction. Comparison of the parameters a, b and d (for definition see below), which point

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54910 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional, isotropic* (Å^2) *and anisotropic* (Å^2) *displacement parameters for cobalt bromine boracite and nickel chlorine boracite*

The form of the temperature factor is $\exp\{-2\pi^2[U(1,1)h^2a^{*2} + U(2,2)k^2b^{*2} + U(3,3)l^2c^{*2} + 2U(1,2)hka^*b^* + 2U(1,3)hla^*c^* + 2U(2,3)klb^*c^*]\}$.

	x	y	z	U
Co1	0.7588 (1)	0.2520 (2)	0.2289 (1)	0.0097 (2)
Co2	0.4882 (1)	0.5254 (1)	0.5012 (1)	0.0102 (3)
Co3	−0.0107 (1)	0.0252 (1)	0.5027 (1)	0.0106 (3)
Br1	0.76434 (7)	0.2494 (2)	0.50870	0.0134 (1)
B1	0.4993 (9)	0.499 (1)	0.2502 (7)	0.001 (2)
B2	0.2568 (7)	0.248 (2)	0.4975 (6)	0.0061 (9)
B3	−0.001 (1)	−0.003 (1)	0.2510 (8)	0.004 (2)
B4	0.4517 (9)	0.251 (1)	0.3499 (5)	0.011 (1)
B5	0.2478 (8)	0.402 (1)	0.1717 (8)	0.005 (2)
B6	0.9050 (7)	0.749 (1)	0.8233 (5)	0.0058 (8)
B7	0.7525 (8)	0.903 (1)	0.6723 (8)	0.004 (2)
O1	0.2329 (5)	0.2501 (8)	0.2425 (4)	0.0054 (7)
O2	0.5415 (6)	0.3295 (5)	0.2749 (4)	0.0062 (7)
O3	0.3794 (6)	0.3292 (5)	0.4338 (4)	0.0078 (8)
O4	0.9682 (6)	0.1640 (5)	0.2693 (4)	0.0054 (7)
O5	0.3224 (6)	0.3625 (4)	0.0654 (4)	0.0060 (7)
O6	0.1685 (6)	0.9730 (5)	0.2308 (4)	0.0075 (7)
O7	0.1394 (6)	0.1724 (5)	0.4265 (4)	0.0082 (8)
O8	0.3340 (5)	0.5195 (5)	0.2296 (4)	0.0052 (7)
O9	0.1705 (6)	0.1271 (4)	0.0650 (4)	0.0056 (7)
O10	0.9512 (6)	0.5914 (5)	0.8455 (4)	0.0071 (7)
O11	0.5414 (6)	0.9110 (4)	0.8528 (4)	0.0063 (7)
O12	0.9111 (6)	0.5421 (4)	0.6502 (4)	0.0046 (7)
O13	0.5893 (6)	0.9415 (4)	0.6554 (4)	0.0054 (7)
Ni1	0.7563 (1)	0.2504 (2)	0.2155 (2)	0.0078 (2)
Ni2	0.4833 (1)	0.5300 (2)	0.4909 (2)	0.0075 (3)
Ni3	−0.0164 (1)	0.0303 (2)	0.4927 (2)	0.0075 (3)
Cl1	0.7903 (2)	0.2507 (3)	0.5087	0.0121 (4)
B1	0.502 (1)	0.502 (2)	0.239 (1)	0.007 (2)
B2	0.2552 (7)	0.247 (2)	0.4877 (7)	0.007 (1)
B3	0.002 (1)	0.000 (2)	0.239 (1)	0.005 (2)
B4	0.4529 (9)	0.251 (1)	0.3390 (6)	0.008 (1)
B5	0.2480 (9)	0.402 (1)	0.158 (1)	0.005 (2)
B6	0.9065 (8)	0.751 (1)	0.8122 (6)	0.008 (1)
B7	0.752 (1)	0.905 (1)	0.660 (1)	0.007 (2)
O1	0.2349 (6)	0.250 (1)	0.2306 (5)	0.0055 (9)
O2	0.5398 (6)	0.3302 (7)	0.2616 (5)	0.007 (1)
O3	0.3806 (6)	0.3315 (6)	0.4245 (5)	0.008 (1)
O4	0.9667 (6)	0.1627 (7)	0.2579 (5)	0.006 (1)
O5	0.3259 (6)	0.3629 (6)	0.0555 (5)	0.007 (1)
O6	0.1700 (7)	0.9725 (7)	0.2203 (5)	0.006 (1)
O7	0.1397 (6)	0.1712 (6)	0.4141 (5)	0.006 (1)
O8	0.3330 (7)	0.5224 (7)	0.2204 (5)	0.005 (1)
O9	0.1694 (6)	0.1253 (6)	0.0543 (5)	0.005 (1)
O10	0.9510 (6)	0.5905 (6)	0.8366 (5)	0.007 (1)
O11	0.5391 (7)	0.9116 (6)	0.8446 (5)	0.008 (1)
O12	0.9136 (6)	0.5446 (6)	0.6391 (5)	0.006 (1)
O13	0.5857 (6)	0.9403 (6)	0.6436 (5)	0.005 (1)

	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Co1	0.0032 (3)	0.0033 (3)	0.0227 (4)	0.0007 (3)	−0.0000 (4)	0.0005 (8)
Co2	0.0107 (5)	0.0093 (3)	0.0106 (5)	−0.0054 (3)	0.0007 (4)	−0.0011 (4)
Co3	0.0106 (5)	0.0079 (3)	0.0135 (5)	−0.0048 (3)	0.0000 (4)	−0.0004 (4)
Br1	0.0128 (3)	0.0096 (2)	0.0176 (3)	0.0001 (3)	−0.0016 (3)	−0.0002 (5)
Ni1	0.0044 (3)	0.0056 (3)	0.0131 (5)	0.0000 (4)	−0.0006 (4)	0.0000 (8)
Ni2	0.0076 (5)	0.0076 (4)	0.0071 (6)	−0.0031 (4)	0.0000 (5)	0.0004 (4)
Ni3	0.0075 (5)	0.0080 (4)	0.0068 (6)	−0.0029 (4)	0.0002 (5)	−0.0002 (4)
Cl1	0.0116 (7)	0.0109 (7)	0.0134 (9)	−0.001 (1)	0.0009 (6)	−0.00 (1)

Table 2. *Lattice parameters a, b, c and d* (Å) *of different boracites,* $M_3B_7O_{13}Hal$ *with* M = Cr, Fe, Co, Ni *and* Cu, *and* Hal = Cl, I *and* Br

d is given by $\frac{1}{2}(c^2 + \{[(a+b)/2]\sqrt{2}\}^2)^{1/2}$.

	Cr Cl*	Fe I	Co Br	Ni Cl	Ni–Br	Cu–Cl
a	8.5659 (3)	8.65879 (4)	8.5614 (2)	8.5105 (4)	8.5218 (2)	8.480 (2)
b	8.6121 (3)	8.65191 (4)	8.5657 (2)	8.4984 (4)	8.5127 (2)	8.440 (2)
c	12.1463 (4)	12.24034 (5)	12.1196 (3)	12.0324 (5)	12.0408 (2)	11.968 (3)
d	8.5889 (3)	8.65529 (4)	8.5667 (2)	8.5063 (4)	8.5157 (2)	8.461 (2)

*At 180 K.

along pseudocubic $[110]_{cub}$ directions, shows that for Ni–Cl, as well as for Ni–Br (Abrahams, Bernstein & Svensson, 1981), Cu–Cl (Uesu, Kobayashi, Anjoh & Schmid, 1978; Thornley, Nelmes & Kennedy, 1976) and Fe–I (Kobayashi, Mizutani, Schmid, & Schachner, 1970) the direction of the *b* axis has the shortest parameter, whereas Co–Br together with Cr–Cl (Mao, Kubel, Schmid & Yvon, 1992) make an exception with the *a* axis being shortest. Half of the pseudocubic face diagonal *d*, given by $\frac{1}{2}(c^2 + \{[(a+b)/2]\sqrt{2}\}^2)^{1/2}$, is always longer than *a* or *b*. This means that squeezing of Co–Br along a pseudocubic [110] direction may lead, under favourable conditions, to a single domain with the *a* axis parallel to the squeezing direction, whereas for the other orthorhombic compounds of Table 2 the *b* axis would be favourable along the squeezing direction. The smaller *a* axis in Co–Br compared to Ni–Cl (and other orthorhombic boracites) is surprising but can be correlated with the position of the halogen atoms. Compared to the ideal position in the cubic structure ($\frac{1}{4}$, $\frac{1}{4}$, *z*) the halogen atoms are mainly shifted in the *x* direction. As can be seen in Table 1, the amount of shift is smaller for the Br (0.12 Å) than for the Cl atom (0.34 Å). This difference of 0.20 Å may explain the smaller *a* axis in Co–Br boracite.

As found for other orthorhombic boracites, the B–O network is broken up at the position of B4 in Co–Br and Ni–Cl, which show nearly triangular surroundings with three short B—O distances of average 1.37 (1) Å for Co–Br and 1.38 (1) Å for Ni–Cl, and one long distance (B4—O1) of 2.280 (8) Å in Co–Br and 2.268 (9) Å in Ni–Cl. The distance between B4 and the (O1, O3, O11) plane is 0.153 (6) Å in Co–Br and 0.156 (7) Å in Ni–Cl. The other B atoms are slightly tetrahedrally distorted, with values of d_{min}/d_{max} for Co—Br and for Ni–Cl following in parentheses ($\sigma_{B-O} = 0.01$) of: B1 1.45/1.52 (1.44/1.52); B2 1.45/1.47 (1.46/1.50); B3 1.46/1.48 (1.44/1.52); B5 1.43/1.56 (1.44/1.56); B6 1.43/1.53 (1.44/1.55); B7 1.45/1.57 (1.44/1.57). The B–O distances are in good agreement for both compounds.

In the orthorhombic phase of iron chlorine, bromine and iodine boracite two different sites of Fe have been detected by means of Mössbauer studies (Schmid & Trooster, 1967; Trooster, 1969). Two quadrupole splittings have been observed indicating two types of Fe^{2+} site with an occupation ratio of 2:1 (Schmid & Trooster, 1967). The compounds under study also show two distinct types of metal atoms. The first type is represented by atoms of Co2 and Co3 (Ni2 and Ni3) and the second type by atoms of Co1 (Ni1). The two types can be distinguished by the temperature factors and the chemical surroundings. The temperature factors of Co2/Ni2 and Co3/Ni3 are identical within 3σ (see Table 1),

Table 3. *Distances* (Å) *between different 'best fits' of* Co3/Co1 *and* Ni3/Ni1 *surroundings compared to the environments of* Co2 *and* Ni2

Co3		Co1		Ni3		Ni1	
Co2—Co3	0.0	—Co1	0.0	—Ni3	0.0	—Ni1	0.0
Br—Br	0.005 (2)	—Br	0.045 (1)	—Cl	0.007 (3)	—Cl	0.027 (2)
O3—O11	0.09 (1)	—O4	0.11 (1)	—O11	0.02 (1)	—O4	0.08 (1)
O5—O13	0.12 (1)	—O2	0.15 (1)	—O13	0.08 (1)	—O2	0.13 (1)
O10—O7	0.08 (1)	—O8	0.24 (1)	—O7	0.13 (1)	—O8	0.21 (1)
O12—O9	0.08 (1)	—O6	0.10 (1)	—O9	0.15 (1)	—O6	0.06 (1)

Table 4. *Metal–halogen and metal–oxygen distances* (Å) *in* $M_3B_7O_{13}Hal$ (M = Co, Ni; *Hal* = Br, Cl)

Co1—Br	2.6759 (13)	Ni1—Cl	2.5197 (19)
O4	2.006 (5)	O4	2.006 (6)
O2	2.052 (5)	O2	2.041 (6)
O8	2.060 (4)	O8	2.039 (6)
O6	2.077 (5)	O6	2.032 (6)
Br*	3.3918 (13)	Cl*	3.5396 (19)
Co2—Br	2.7203 (15)	Ni2—Cl	2.494 (3)
O12	2.008 (5)	O12	1.984 (6)
O10	2.037 (5)	O10	2.006 (6)
O5	2.039 (5)	O5	2.017 (6)
O3	2.087 (4)	O3	2.061 (6)
Br*	3.3447 (15)	Cl*	3.536 (3)
Co3—Br	2.7210 (15)	Ni3—Cl	2.501 (3)
O7	2.023 (5)	O7	2.023 (5)
O9	2.035 (5)	O9	1.998 (5)
O13	2.058 (5)	O13	2.029 (6)
O11	2.080 (5)	O11	2.057 (6)
Br*	3.3292 (15)	Cl*	3.543 (3)

*From symmetry equivalent halogen.

whereas those for Co1/Ni1 are different. The metal sites of Co2/Ni2 and Co3/Ni3 atoms have similar oxygen and halogen environments compared to the surroundings of the Co1/Ni1 atom. The two types of surroundings were compared by superimposing the $M(n)$–$O_4(n)$–halogen 'molecules' calibrated to identical metal positions using an X-ray routine (Hall & Stewart, 1990). The distances between the O and Br/Cl atoms of the two 'molecules' Ni–O_4–Cl and Co–O_4–Br were calculated. The best superposition was found for the 'molecules' around Ni2 and Ni3 and Co2 and Co3 mainly for the metal–halogen distances. Distances between different fits are listed in Table 3. It should be noted that the three metal sites are crystallographically inequivalent, but two of them, (2) and (3), are very similar owing to an approximately parallel shift of both halogens of the O_4X_2 octahedron along a single [111] direction upon the cubic→orthorhombic transition, whereas for site (1) the two halogens move along different [111] directions, forming an angle of about 109° with one another [see Fig. 9 in Schmid (1970)]. Interatomic distances around the metal atoms are listed in Table 4.

The structural similarity of sites (2) and (3) found for Ni–Cl and Co–Br boracite is also reflected in the Mössbauer spectra of the analogous phases of Fe–Cl, Fe–Br and Fe–I boracite, *i.e.* the quadrupole splittings for sites (2) and (3) are indistinguishable, whereas that of site (1) is notably different (Schmid & Trooster, 1967; Trooster, 1969). Contrary to the Mössbauer effect, EPR measurements on the analogous orthorhombic phases of Mg–Cl boracite (Dowty & Clark, 1973) and Zn–Cl boracite, using Mn^{2+} as a probe, clearly showed separate spectra (here with distinct spin Hamiltonian parameters E, D and $\lambda = E/D$) for sites (1), (2) and (3), proving clearly the crystallographically inequivalent environments (Rivera, Bill & Lacroix, 1976; Rivera, 1976). By combining EPR, X-ray and birefringence measurements, it was even possible to correlate the individual EPR spectra with sites (1), (2) and (3) (Rivera, Bill & Lacroix, 1988); however, so far it has not been possible to establish a one to one correspondence between the details of the local environment of the metal ion and the magnitude of the spin Hamiltonian parameters.

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