Cubic structure of chromium-bromine boracite at 298 and 113 K

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Abstract

Cr$_3$B$_7$O$_3$Br, $M_r$ = 519.55, cubic, F43c, $Z = 8$, a(Mo Ka) = 0.71073 Å, $F(000) = 1968$. At 298 K: $a = 12.1524$ (1) Å, $V = 1794.68$ (3) Å$^3$, $D_x = 3.845$ Mg m$^{-3}$, $\mu = 8.533$ mm$^{-1}$, final $R = 0.020$ for 206 unique reflections with $I > 3/\sigma(I)$; shortest interatomic distances (Å): Cr--O = 2.061 (2), Cr--Br = 3.03810 (3), B--O = 1.436 (3), O--O = 2.388 (2). At 113K: $a = 12.1340$ (3) Å, $V = 1786.54$ (13) Å$^3$, $D_x = 3.863$ Mg m$^{-3}$, $\mu = 8.533$ mm$^{-1}$, final $R = 0.025$ for 281 unique reflections with $I > 3/\sigma(I)$; shortest interatomic distances (Å): Cr--O = 2.057 (2), Cr--Br = 3.0335 (1), B--O = 1.436 (3), O--O = 2.390 (2). The planarity of the metal-centred CrO$_4$ groups does not differ significantly from that in other chromium-based cubic boracites and generally increases as the temperature is lowered.

Reference


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Cubic Structure of Chromium–Bromine Boracite at 298 and 113 K

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Abstract

Cr₃B₇O₁₃Br, \( M_r = 519.55 \), cubic, \( Fd\bar{3}c \), \( Z = 8 \), \( \lambda(Mo \text{ } K\alpha) = 0.71073 \text{ \AA} \), \( F(000) = 1968 \). At 298 K: \( a = 12.1524 (1) \text{ \AA} \), \( V = 1794.68 (3) \text{ \AA}^3 \), \( D_r = 3.845 \text{ Mg m}^{-3} \), \( \mu = 8.533 \text{ mm}^{-1} \), final \( R = 0.020 \) for 206 unique reflections with \( I > 3\sigma(I) \); shortest interatomic distances (\( \text{\AA} \)): Cr–O = 2.061 (2), Cr–Br = 3.0381 (3), Br–O = 1.436 (3), O–O = 2.388 (2). At 113 K: \( a = 12.1340 (3) \text{ \AA} \), \( V = 1786.54 (13) \text{ \AA}^3 \), \( D_r = 3.863 \text{ Mg m}^{-3} \), \( \mu = 8.533 \text{ mm}^{-1} \), final \( R = 0.025 \) for 281 unique reflections with \( I > 3\sigma(I) \); shortest interatomic distances (\( \text{\AA} \)): Cr–O = 2.057 (2), Cr–Br = 3.0335 (1), B–O = 1.436 (3), O–O = 2.390 (2). The planarity of the metal-centred CrO₄ groups does not differ significantly from that in other chromium-based cubic boracites and generally increases as the temperature is lowered.

Introduction

So far the cubic phases of seven boracites \( M_3B_7O_{13}X \) (\( M = \text{bivalent metal ion}, X = \text{halogen ion} \)) based on 3d transition elements, \( M = \text{Cr, Co, Ni, Cu} \), have been structurally characterized [for a review see Nelmes (1974); for later work see Monnier, Berset, Schmid & Yvon (1987), and references therein]. The metal ions in these structures are tightly bound to four nearly planar oxygen atoms and loosely bound to two apical halogen atoms. Most boracites (hereafter \( M-X \)) undergo structural phase transitions to non-cubic low-temperature modifications in which all (or part) of the metal ions strongly attract one of the halogen ligands. The known transition temperatures are situated between 60 K (Ni-I; Schmid, 1965) and 797 K (Cd-CI; Schmid & Tippmann, 1978). With a view to investigating the factors responsible for this large temperature range we have decided to study cubic Cr₃B₇O₁₃Br (hereafter Cr-Br). This compound together with Cr-I and Cu-I make up the exceptional and sole boracite compositions for which no structural transition to a non-cubic phase occurs down to very low temperature. This has been verified by observation in polarized light down to 10 K for Cr-Br and Cr-I (Schmid, 1965), reconfirmed for Cr-Br down to 9 K (Ye, 1991), and down to 15 K for Cu-I (Monnier et al., 1987).

Experimental

Blue cube-shaped Cr-Br crystals were grown by the chemical vapour transport method (Schmid, 1965). Data collection: CAD-4 automatic four-circle diffractometer, graphite monochromator, liquid-
Table 1. Fractional atomic coordinates \((\times 10^4)\) and equivalent isotropic displacement parameters \((\text{Å}^2 \times 10^4)\) at 298 K (first line) and 113 K (second line)

\[ U_{eq} = \frac{1}{3} \text{tr}(U) \]

Space group \(\text{F}7\bar{3}c\), e.s.d.'s in parentheses.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>24(c)</td>
<td>0</td>
<td>2500</td>
</tr>
<tr>
<td>Br</td>
<td>8(b)</td>
<td>0</td>
<td>2500</td>
</tr>
<tr>
<td>B(I)</td>
<td>24(d)</td>
<td>2500</td>
<td>0</td>
</tr>
<tr>
<td>B(2)</td>
<td>32(e)</td>
<td>798</td>
<td>2</td>
</tr>
<tr>
<td>O(1)</td>
<td>8(a)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(2)</td>
<td>96(h)</td>
<td>196</td>
<td>(I)</td>
</tr>
</tbody>
</table>

Table 2. Interatomic distances (Å) and deviation from planarity, \(\varepsilon\) (Å), of the metal-centred \(\text{CrO}_4\) groups in cubic \(\text{Cr-X}\) (\(X=\text{halogen}\)) boracites, with e.s.d.'s in parentheses

<table>
<thead>
<tr>
<th>(\varepsilon)</th>
<th>(\text{Cr-CI}^*)</th>
<th>(\text{Cr-Br}^+)</th>
<th>(\text{Cr-I}^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(298\text{ K})</td>
<td>0.241 (1)</td>
<td>0.238 (1)</td>
<td>0.231 (1)</td>
</tr>
<tr>
<td>(113\text{ K})</td>
<td>0.238 (1)</td>
<td>0.235 (1)</td>
<td>0.233 (1)</td>
</tr>
</tbody>
</table>

† This work.
§ Shortest contact distance.

Results and discussion

The chromium atoms in \(\text{Cr-Br}\) are coordinated by four close oxygen atoms in a nearly square-planar configuration, and by two distant apical halogen atoms (Fig. 1). The bond distances, \(\text{Cr-O=2.061 (2)}\, \text{Å at room temperature}\), increase as a function of ionic size of the halogens and decrease as the temperature is decreased. By comparison, the boron-oxygen bond distances and oxygen-oxygen contact distances change only little, thus confirming the picture of a relatively rigid oxygen–boron network.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54612 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
As expected from the topology of the boracite structure and its bonding, the metal ions vibrate mainly along the fourfold axis \( i.e. \) in directions parallel to the weak metal–halogen bonds and perpendicular to the strong metal–oxygen bonds. Within the chromium-based series the anisotropy of the displacement amplitudes is largest for Cr-Cl, \( \langle u^2 \rangle / \langle u^2 \rangle_p = 5.1 \) (Table 3). It decreases with increase of the ionic size of the halogens but does not vary significantly as a function of temperature. There is also no significant difference between the temperature dependence of the displacement amplitudes in a boracite that is structurally stable such as Cr-Br and in one that is structurally unstable such as Ni-I \( (T_i = 60 \text{ K}) \).

The deviation from planarity of the \( \text{CrO}_4 \) groups in Cr-Br, \( \epsilon \), does not differ significantly from that in the other chromium-based boracites Cr-Cl and Cr-I, but decreases as the temperature is lowered. This is surprising in view of the overall trend of \( \epsilon \) that increases with the cubic cell parameter, \( a \), as suggested by Monnier et al. (1987), and illustrated in Fig. 2. Notice that for a given temperature \( a \) does not always correlate with the size of the halogens, as can be seen, for example, with the copper-based boracites Cu-Br and Cu-I. These observations can be taken as further evidence for the contribution of the transition element to the complex atomic interactions in boracites. For example, Jahn–Teller-active ions such as \( \text{Cu}^{2+} (d^9) \) and \( \text{Cr}^{2+} (d^4) \) could contribute to preserve a square-planar oxygen environment around the transition metal. This could decrease the tendency toward a structural phase transition and explain the absence of such a transition in Cr-Br, Cr-I and Cu-I. In other boracites this transition usually changes the square-planar metal coordination to a square-pyramidal one. Theoretical calculations and further structural data are necessary to confirm this hypothesis.

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**References**


