bzw. 1,618 Å (unkorrigiert) und stimmt damit innerhalb der Fehlergrenzen mit den für $KMnO_4$ (1,629 Å) und $AgMnO_4$ (1,633 Å) bestimmten Werten überein (Palenik, 1967*a*; Chang & Jansen, 1984). Bezogen auf die gemittelten Mn—O-Abstände ist somit innerhalb der Fehlerbreite kein Einfluss der einwertigen Kationen erkennbar.

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Structure of Boracite $Cu_3B_7O_{13}I$

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Abstract. $M_r = 601{\cdot}07$, cubic, $F\bar{4}3c$, $a = 12{\cdot}0203\,(7)$ Å, $V = 1736{\cdot}9\,(1)$ Å^3, $Z = 8$, $D_x = 4{\cdot}608$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 9{\cdot}99$ mm^{-1}, $F(000) = 2232$, $T = 298$ K, final $R = 0{\cdot}014$ for 110 unique reflections. This new boracite has been prepared by high-pressure synthesis; its structure is comparable with that of other cubic boracites. No structural phase transition could be observed between 15 and 1265 K.

Introduction. It is well known that, in spite of many attempts, the existence of CuI_2 has never been proved (Jørgensen, 1965, 1970). In consequence, the traditional route to synthesize boracites (Schmid, 1965) was not successful for obtaining $Cu_3B_7O_{13}I$, owing to the fact that this method involves gas-phase transport with the metal(II) halides operating as reaction intermediates. Therefore, it was interesting to find out whether Cu^{2+} and I^- could perhaps be incorporated under high pressure into a borate framework, forming the boracite of composition $Cu_3B_7O_{13}I$.

A method for preparing boracites, using high pressure applied to condensed phases, has been introduced by Bither & Young (1974). Recently, we have employed this method to obtain large single crystals of $Co_3B_7O_{13}F$, enabling us to determine the structure and some of the properties of this boracite (Berset, Yvon, Depmeier, Boutellier & Schmid, 1984). The present paper reports now the successful high-pressure synthesis of $Cu_3B_7O_{13}I$ (hereinafter called Cu—I) and the results of the structure refinement.

Experimental. The synthesis is a version of the procedure described by Bither & Young (1974), adapted to our laboratory: six-anvil press, cube-shaped high-pressure cell; starting materials: stoichiometric mixtures of CuI (*purum*, Fluka), CuO (specpure, Johnson Matthey Chemicals), I_2 (*puriss p.a.*, Fluka), B_2O_3 (puratronic, Johnson Matthey Chemicals) and 15% excess B_2O_3 as H_3BO_3 (*pro analysi*, Merck), typical total weight 770 mg; platinum crucible; hydrostatic pressure of 25 $\times 10^8$ Pa; 1132 K for 2 h; cooling rate 100 K h^{-1}; quenching after 3·5 h. Yellowish-brown idiomorphic crystals; facets {100}, {110} and {111}; maximum size 200 µm. Refractive index (1·92), measured by the immersion technique; good agreement (1·924) with the result obtained employing the Gladstone–Dale equation (Mandarino, 1981), using an estimated value for the Gladstone–Dale constant of CuI_2 obtained by interpolation between those of NiI_2 and ZnI_2.

No phase transition was found up to 1265 K by means of differential thermal analysis (Mettler TA-2000), and down to 15 K by means of optical observation under polarized light.

Data collection: regularly shaped crystal, approximately 0·1 mm ∅; Philips PW 1100 diffractometer, graphite monochromator; one hemisphere ($-13 \leq h,k \leq 13$), $(\sin\theta/\lambda)_{\max} = 0{\cdot}5719$ Å^{-1}; ω–2θ scan, scan width 0·9°, scan speed 0·03° s^{-1}; background measured on both sides of the reflection for half the scan time used for the peak; two standard reflections after every 120 min (no significant change);

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

E.s.d.'s are in parentheses. $U_{eq} = \frac{1}{3}$ trace **U**.

	Wyckoff notation	x	y	z	U_{eq}
Cu	24(c)	2500	2500	0	8 (1)
I	8(b)	2500	2500	2500	8 (1)
B(1)	24(d)	2500	0	0	4 (2)
B(2)	32(e)	813 (6)	813 (6)	813 (6)	10 (1)
O(1)	8(a)	0	0	0	5 (1)
O(2)	96(h)	1807 (3)	182 (3)	991 (3)	4 (1)

1596 reflections; Lorentz and polarization corrections, no absorption correction ($\mu R \simeq 0{\cdot}1$); lattice parameter (least squares) from a previous Guinier photograph (Cu $K\alpha_1$); $R_{int} = 0{\cdot}043$, R_{int}(weighted) = 0·048.

Structure refinement: preliminary coordinates from $Cu_3B_7O_{13}Cl$ (Thornley, Nelmes & Kennedy, 1976); full-matrix least squares; $\sum w(|F_o| - |F_c|)^2$ minimized; scattering factors for neutral atoms; 21 variables included one scale factor, one isotropic-extinction parameter, one enantiomorph-polarity parameter (Flack, 1983) as well as 4 positional and 14 anisotropic thermal parameters. Of 116 unique reflections, 6 were 'less-thans' calculating smaller than the 'less-thans' threshold [$I < 3\sigma(I)$] and did not contribute to the refinement. With 110 reflections and unit weights the final R and wR were 0·014 and 0·016, respectively. $(\Delta/\sigma)_{max} = 0{\cdot}1$. A difference Fourier map calculated after the final least-squares cycle was featureless. All calculations performed with the *XRAY76* system of programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a Univac 1100 computer.

Discussion. Table 1 contains the final positional parameters and equivalent isotropic temperature-factor coefficients.* Cu—I has all the structural characteristics of cubic boracites (Nelmes & Thornley, 1974; Sueno, Clark, Papike & Konnert, 1973; Thornley, Nelmes & Kennedy, 1976; Nelmes & Thornley, 1976; Nelmes & Hay, 1981); in particular, the Cu^{2+} ion is pseudo-octahedrally coordinated by four O and two I atoms, the O(1) atom is tetrahedrally coordinated by B atoms and all B atoms have tetrahedral coordination spheres.

The lattice parameters as well as the M—O and M—X distances decrease in the series Co—I, Ni—I and Cu—I in accordance with ionic radii (Wells, 1975). The same trend is observed in the series Cu—I, Cu—Br, Cu—Cl, whereby the lattice parameter of the latter has been estimated from a Guinier photograph taken at room temperature, because this boracite is cubic only above 390 K.

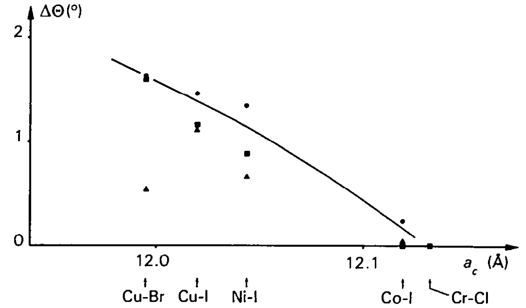

Fig. 1. The differences of the torsion angles [O(1)–B(2)–O(2)–B(1),●], [B(2)–O(1)–B(2)–O(2),▲] and [B(2)–O(2)–B(1)–O(2),■] from the corresponding ones in the Cr–Cl boracite as a function of the lattice parameters (representing the composition) for some cubic boracites.

In order to clarify whether there exists an expected correlation between the composition of a boracite and its framework geometry, the torsion angles have been calculated for rings which form chains within the framework, running along ⟨100⟩ and which are linked by common B(1) and O(1) atoms. The differences of these angles from the corresponding ones in the Cr—Cl boracite have been plotted as a function of the lattice parameters (representing the composition) for several cubic boracites (Fig. 1). Indeed, a general trend is observed, *viz* that increasing torsion angles are accompanied by decreasing lattice parameters and *vice versa*. This proves that the response of the borate framework to different non-framework ions, expressed by the lattice parameter, is due to some cooperative movement of the polyhedra which make up the framework. Cu—Br boracite does not strictly follow the general tendency; this might well indicate that the relationship between lattice parameters and framework distortion is not a simple one.

No phase transition has been found between 15 and 1265 K, where the crystals decompose forming CuB_2O_4.

The six-anvil press was provided by the Département de Physique de la Matière Condensée (Genève); the X-ray equipment and the computer programs were made accessible by the Laboratoire de Cristallographie aux Rayons X, Genève. This work was supported by the Swiss National Science Foundation under contract number 2.833–0.83.

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Structure of $Na_2Ba_3Cr_4F_{20}$

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Abstract. $M_r = 1045{\cdot}9$, monoclinic, $P2_1/n$, $a = 7{\cdot}262\,(4)$, $b = 20{\cdot}668\,(8)$, $c = 5{\cdot}431\,(2)$ Å, $\beta = 90{\cdot}76\,(1)°$, $V = 815{\cdot}1$ Å^3, $Z = 2$, $D_x = 4{\cdot}26$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 98{\cdot}9$ cm^{-1}, $F(000) = 931{\cdot}93$, room temperature, $R = 0{\cdot}027$, 1099 unique reflections. The structure is built from infinite *cis* $[MF_5^{2-}]$ chains of corner-sharing octahedra as in the $BaGaF_5$ structure. A valence-bond analysis shows that an Na^+ ion is mainly bonded to only one chain whereas the Ba^{2+} ions ensure the connection between several chains.

Introduction. The only type of phase previously reported in the ternary systems Na–BaF_2–MF_3 is $NaBaM_2F_9$ (M^{III} = Fe, Cr, Ga, Al) (de Kozak, Samouël, Leblanc & Ferey, 1982). It was recently found to crystallize (Ferey, Leblanc, de Kozak, Samouël & Pannetier, 1985) with the Ba_2CoFeF_9-type structure (de Kozak, Leblanc, Samouël, Ferey & De Pape, 1981).

This paper reports the single-crystal structure determination of a new phase of these ternary diagrams: $Na_2Ba_3Cr_4F_{20}$. Its one-dimensional structure is related to that of $BaCrF_5$ (Holler, Kurtz, Babel & Knop, 1982) and is compared with that of $NaBaM_2F_9$ in terms of a valence-bond analysis.

Experimental. Single crystal grown by heating the elementary fluorides at $T = 1173$ K in a platinum tube for 72 h. D_m not determined. Green crystal $0{\cdot}210 \times 0{\cdot}045 \times 0{\cdot}045$ mm. Data collected on an automatic four-circle Philips PW 1100 diffractometer, θ–2θ scan mode, sweep 1·40°, aperture 1·0°, scanning speed $0{\cdot}03°\,s^{-1}$. Cell parameters from 25 reflections. Absorption corrections by the Gauss method; $A_{max} = 0{\cdot}610$, $A_{min} = 0{\cdot}177$. Intensity measurement to $\theta_{max} = 25°$ within range $-9 \leq h \leq +9$, $0 \leq k \leq 25$, $-6 \leq l \leq +6$; standard reflections $\bar{1}\bar{4}1$, $1\bar{4}1$, $\bar{2}1\bar{1}$, intensity variation 2·5%; 2310 reflections measured, 579 rejected $[\sigma(I)/I > 0{\cdot}5]$, 1099 unique $[|F|/\sigma(|F|) > 6{\cdot}0]$, $R_{int} = 0{\cdot}034$. Structure solved from tangent method. F magnitudes used in least-squares refinements; unit weights; 134 parameters refined; mean $\Delta/\sigma = 0{\cdot}013$, max. $= 0{\cdot}080$; secondary-extinction factor $g = 2{\cdot}60\,(9) \times 10^{-7}$. Atomic scattering factors for Na^+, Ba^{2+}, Cr^{3+}, F^- and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); calculations with *SHELX*76 program (Sheldrick, 1976); max. and min. heights in final ΔF map: 1·1 and −0·9 e Å^{-3}.

Discussion. The final atomic coordinates and the equivalent isotropic temperature factors are listed in Table 1.† Projections of the structure along [001] and [010] appear in Figs. 1 and 2, respectively.

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† Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42409 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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