Structure of boracite Cu3B7O13I

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Abstract

Cu3B7O13I is cubic, space group F̅43c, with a 12.0203(7) Å; d.(calcd.) = 4.608 for Z = 8. Final R = 0.014 for 110 unique reflections. At. parameters are given. 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.

Reference


DOI : 10.1107/S0108270185009106
bzw. 1,618 Å (unkorrigiert) und stimmt damit innerhalb der Fehlergrenzen mit den für KMnO₄ (1,629 Å) und AgMnO₄ (1,633 Å) bestimmten Werten überein (Palenik, 1967a; Chang & Jansen, 1984). Bezogen auf die gemittelten Mn—O-Abstände ist somit innerhalb der Fehlerbreite kein Einfluss der einwertigen Kationen Ag⁺, Mn²⁺ festzustellen.

Literatur


Structure of Boracite Cu₃B₇O₁₃I

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Abstract. Mₚ = 601.07, cubic, F43c, a = 12.0203 (7) Å, V = 1736.9 (1) Å³, Z = 8, D = 4.608 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 9.99 mm⁻¹, F(000) = 2232, T = 298 K, final R = 0.014 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 CuI₂ has never been proved (Jørgensen, 1965, 1970). In consequence, the traditional route to synthesize boracites (Schmid, 1965) was not successful for obtaining Cu₃B₇O₁₃I, 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 Cu²⁺ and I⁻ could perhaps be incorporated under high pressure into a borate framework, forming the boracite of composition Cu₃B₇O₁₃I.

A method for preparing boracites, using high pressure applied to condensed phases, has been introduced 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), I₂ (puriss p.a., Fluka), B₂O₃ (puratronic, Johnson Matthey Chemicals) and 15% excess B₂O₃ as H₃BO₃ (pro analysis, Merck), typical total weight 770 mg; platinum crucible; hydrostatic pressure of 25 × 10⁸ Pa; 1132 K for 2 h; cooling rate 100 K h⁻¹; quenching after 3.5 h. Yellowish-brown idiomorphic crystals; faces {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 CuI₂ obtained by interpolation between those of NiI₂ and ZnI₂.

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 2; Philips PW 1100 diffractometer, graphite monochromator; one hemisphere (−13 ≤ h,k ≤ 13), (sinθ/λ)ₘₐₓ = 0.5719 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);
Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($A^2 \times 10^3$)

\[
\begin{array}{cccccc}
\text{Wyckoff} & \text{notation} & \text{x} & \text{y} & \text{z} & \text{Ueq} \\
\text{Cu} & 24(e) & 2500 & 2500 & 0 & 8(1) \\
\text{I} & 8(b) & 2500 & 2500 & 2500 & 8(1) \\
\text{B(1)} & 24(d) & 2500 & 0 & 0 & 4(2) \\
\text{B(2)} & 32(e) & 813(6) & 813(6) & 813(6) & 10(1) \\
\text{O(1)} & 8(a) & 0 & 0 & 0 & 5(1) \\
\text{O(2)} & 96(h) & 1807(3) & 182(3) & 991(3) & 4(1)
\end{array}
\]

E.s.d.'s are in parentheses. \(U_{eq} = \frac{1}{3} \text{trace } U\).

1596 reflections; Lorentz and polarization corrections, no absorption correction ($\mu R \approx 0.1$); lattice parameter (least squares) from a previous Guinier photograph ($Cu K\alpha_1$); \(R_{int} = 0.043\), \(R_{int}(\text{weighted}) = 0.048\).

Structure refinement: preliminary coordinates from Cu$_2$B$_2$O$_5$Cl (Thornley, Nelmes & Kennedy, 1976); full-matrix least squares; $\Sigma w(F_0^2 - |F_c|)^2$ 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. $(\Delta/\sigma)_{max} = 0.1$. 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 $M$—I 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.

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 $\langle 100 \rangle$ 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 Cu$_2$B$_2$O$_5$.

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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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42416 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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References


Structure of Na₂Ba₃Cr₄F₂₀

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(Received 18 March 1985; accepted 29 July 1985)

Abstract. $M_r = 1045.9$, monoclinic, $P2_1/n$, $a = 7.262$ (4), $b = 20.668$ (8), $c = 5.443$ (2) Å, $\beta = 90.76$ (1)°, $V = 815.1$ Å³, $Z = 2$, $D_x = 4.26$ g cm⁻³, $\text{Mo K} \alpha$, $\lambda = 0.71069$ Å, $\mu = 98.9$ cm⁻¹, $F(000) = 931.93$, room temperature, $R = 0.027$, 1099 unique reflections. The structure is built from infinite cis $[\text{MF}_2^2]^{-}$ chains of corner-sharing octahedra as in the BaGaF₅ structure. A valence-bond analysis shows that an Na⁺ ion is mainly bonded to only one chain whereas the Ba²⁺ ions ensure the connection between several chains.

Introduction. The only type of phase previously reported in the ternary systems Na–BaF₂–MF₃ is NaBa₅M₂F₁₈ ($M^{III} = \text{Fe, Cr, Ga, Al}$) (de Kozak, Samouël, Leblanc & Ferey, 1982). It was recently found to crystallize (Ferey, Leblanc, de Kozak, Samouël & Pannetier, 1985) with the Ba₅CoFeF₉-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: Na₂Ba₃Cr₄F₂₀. Its one-dimensional structure is related to that of BaCrF₅ (Holler, Kurtz, Babel & Knop, 1982) and is compared with that of NaBaM₂F₉ 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 0·210 × 0·045 × 0·045 mm. Data collected on an automatic four-circle Philips PW 1100 diffractometer, $\theta$–$2\theta$ scan mode, sweep 1·4°, aperture 1·0°, scanning speed 0·03° s⁻¹. Cell parameters from 25 reflections. Absorption corrections by the Gauss method; $A_{\text{max}} = 0·610$, $A_{\text{min}} = 0·177$. Intensity measurement to $\theta_{\text{max}} = 25°$ within range $-9 \leq h \leq +9$, $0 \leq k \leq 25$, $-6 \leq l \leq +6$; standard reflections 141, 141, 211, intensity variation 2·5%; 2310 reflections measured, 579 rejected [$|F|/|I| > 0·5$, 1099 unique $|F|/\sigma(|F|) > 6·0$], $R_{\text{int}} = 0·034$. Structure solved from tangent method. $F$ magnitudes used in least-squares refinements; unit weights; 134 parameters refined; mean $\Delta f/\sigma = 0·013$, max. = 0·080; secondary-extinction factor $g = 2·60 (9) \times 10^{-7}$. Atomic scattering factors for Na⁺, Ba²⁺, Cr³⁺, F⁻ and anomalous-dispersion corrections from International Tables for X-ray Crystallography (1974); calculations with SHELX76 program (Sheldrick, 1976); max. and min. heights in final $\Delta F$ 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.

† 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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