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How to cite

MAO, Shao Yu et al. Powder and single-crystal x-ray study of chromium chlorine boracite, $Cr_3B_7O_{13}Cl$, at low temperature. Powder refinement of the orthorhombic modification at 100 K. In: Ferroelectrics, 1992, vol. 132, n° 1-4, p. 239–244.

Ferroelectrics, 1992, Vol. 132, pp. 239–244
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POWDER AND SINGLE-CRYSTAL X-RAY STUDY OF CHROMIUM CHLORINE BORACITE, $Cr_3B_7O_{13}Cl$, AT LOW TEMPERATURE. POWDER REFINEMENT OF THE ORTHORHOMBIC MODIFICATION AT 100 K

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(Received October 1, 1991; in final form November 12, 1991)

$Cr_3B_7O_{13}Cl$: $Pca2_1$, $a = 8.5647(2)$ Å, $b = 8.6125(2)$ Å, $c = 12.1453(3)$ Å, $V = 895.88(6)$ Å^3, $D_x = 3.522$ g.cm^{-3}, $R_p = 0.0273$ and $R_B = 0.0723$ for 54 reflections and 63 parameters as refined from X-ray powder profile data at $T = 100$ K. Lattice parameters as measured on single-crystals and powders show a discontinuous volume increase of 0.45% at the cubic-to-tetragonal phase transition at 264 K, but practically no volume change (<0.01%) at the tetragonal-to-orthorhombic phase transition at 180 K. The metal coordinations in the orthorhombic low-temperature modification differ less from those in the cubic high-temperature modification than in other boracites.

INTRODUCTION

Boracites, $M_3B_7O_{13}X$ (M = divalent metal ion, X = halogen) usually undergo a series of phase transitions from a paraelectric cubic high-temperature (HT) modification to various ferroelastic/ferroelectric rhombohedral, orthorhombic and monoclinic low-temperature (LT) modifications.[1] $Cr_3B_7O_{13}Cl$ (hereafter Cr—Cl) is an exception as it transforms first from the face-centered cubic HT modification (space group $F\bar{4}3c$) to a primitive tetragonal ferroelastic/antiferroelectric LT modification (space group $P\bar{4}2_1c$, quadrupled primitive cubic cell volume, $T_1 = 264$ K), and then to a primitive orthorhombic LT modification (space group $Pca2_1$, doubled primitive cubic cell volume, $T_2 = 160$ K).[2–5] The structure of the tetragonal LT modification has recently been determined by X-ray diffraction on a single-domain crystal.[3] Here we report the structure of the orthorhombic LT modification as refined from an X-ray powder diffraction study.

EXPERIMENTAL AND RESULTS

A single-domain crystal of the orthorhombic modification of Cr—Cl could not be obtained. Thus a single crystal was selected under the microscope, cleaned in boiling

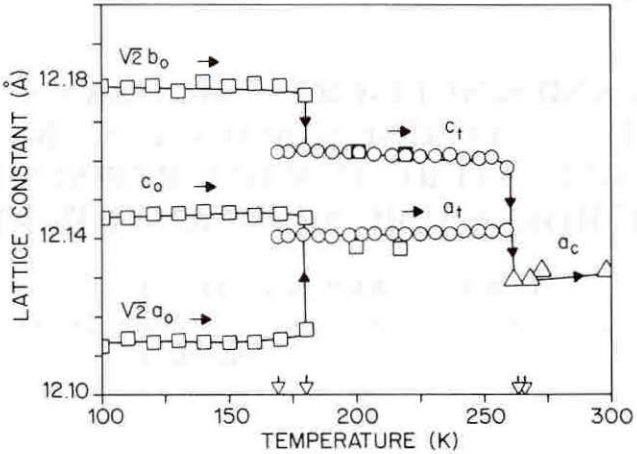

FIGURE 1 Lattice parameters of chromium-chlorine boracite as a function of temperature between 100 K and 300 K during heating. Squares indicate the parameters obtained from powder diffraction in the orthorhombic (a_0, b_0, c_0) and tetragonal phases (a_t, c_t), circles and triangles denote the parameters obtained from single crystal diffraction in the tetragonal (a_t, c_t) and cubic phase (a_c), respectively. The bold arrows indicate the direction of the measurements, the open arrows the width of phase transition hysteresis. The size of the symbols corresponds to 3 times e.s.d.

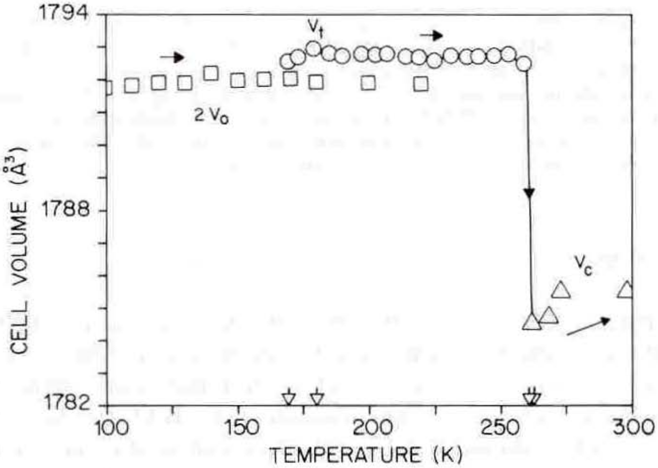

FIGURE 2 The cell volumes of the orthorhombic (V_0), tetragonal (V_t) and cubic (V_c) modifications of chromium-chlorine boracite as a function of temperature between 100 K and 300 K during heating.

water and then ground into a fine powder. In order to relieve mechanical stress the powder was treated in an ultrasonic bath. It was investigated on a high-resolution Guinier powder diffractometer equipped with a closed-cycle helium refrigerator[6] (Ge monochromator, λ ($CuK\alpha_1$) = 1.54056 Å). High-precision lattice parameters of the orthorhombic phase were obtained by cooling to temperatures between 100 K to 180 K in steps of 10 K, and measuring diffraction patterns from $\theta = 5°$ to $\theta = 50°$ in steps of 0.005° by using silicon (a = 5.43083 Å; T = 300 K) as an internal standard. For the sake of comparison lattice parameters were also measured for the tetragonal phase at two temperatures (200 K and 220 K). The results are presented in Figures 1 and 2.

TABLE I

The atomic parameters of orthorhombic $Cr_3B_7O_{13}Cl$ boracite from X-ray powder diffraction refinement at 100 K; space group $Pca2_1$, all atoms in 4a; estimated standard deviations of Cr, Cl and O atoms are indicated in parentheses, the *z* position of Cl atom was fixed at 0.5 during the refinements, the "e.s.d." indicated for B atoms were determined by fixing all other positions

$Pca2_1$	x	y	z	U_{iso} (×100Å^2)
Cr(1)	.7281(7)	.249(1)	.2649(6)	1.78(4)
Cr(2)	.502(2)	.491(1)	.5024(9)	1.78(4)
Cr(3)	-.004(1)	-.010(1)	.001(1)	1.78(4)
Cl	.743(2)	.246(2)	.5	2.5(1)
B(1)	.494(6)	.506(4)	.247(4)	#
B(2)	.267(4)	.236(6)	.495(3)	#
B(3)	.006(6)	-.014(4)	.236(4)	#
B(4)	.416(4)	.297(4)	.330(3)	#
B(5)	.238(5)	.448(4)	.163(3)	#
B(6)	.911(3)	.721(5)	.821(3)	#
B(7)	.753(5)	.905(4)	.674(3)	#
O(1)	.283(2)	.265(3)	.272(2)	#
O(2)	.532(2)	.331(2)	.258(2)	#
O(3)	.356(2)	.325(3)	.432(2)	#
O(4)	.959(2)	.177(2)	.287(2)	#
O(5)	.349(3)	.361(3)	.057(2)	#
O(6)	.199(2)	.987(3)	.232(2)	#
O(7)	.112(2)	.166(3)	.432(2)	#
O(8)	.335(2)	.527(2)	.239(2)	#
O(9)	.167(3)	.140(3)	.069(2)	#
O(10)	.959(3)	.579(3)	.833(2)	#
O(11)	.566(2)	.901(2)	.829(2)	#
O(12)	.898(3)	.553(3)	.644(2)	#
O(13)	.602(3)	.974(3)	.639(2)	#

U_{iso}, Isotropic displacement parameters.
#, Parameter fixed at 0.

For the structure refinement of the orthorhombic phase a powder diffraction profile was recorded at 100 K without a Si standard, by step-scanning from 5° to 50°, with increments of 0.005° and a counting time of 30 seconds per step. The background was subtracted manually. The structure refinement was based on an orthorhombic model[7] described in space group $Pca2_1$, by using a modified version of the DBW3.2S programme.[8] A total of 63 variables was refined: one zeropoint, one scale factor, three halfwidth parameters, one pseudo-Voigt profile parameters, one asymmetry parameter, one preferred orientation parameter, three lattice parameters, 50 atomic and two isotropic displacement parameters for Cr, Cl, and O.

TABLE II

Bond distances (Å) of orthorhombic chromium-chlorine boracite at 100 K (e.s.d.'s in parentheses)

Cr(1) --	Cl	2.858(7)	Cr(3) --	Cl	2.93(2)
	Cl	3.227(7)		Cl	3.09(2)
	O(2)	1.83(2)		O(13)	1.92(3)
	O(6)	2.08(2)		O(9)	1.97(3)
	O(4)	2.08(2)		O(7)	2.00(3)
	O(8)	2.15(2)		O(11)	2.30(3)
Cr(2) --	Cl	2.96(2)	Cl --	Cr(1)	2.858(7)
	Cl	3.17(2)		Cr(3)	2.93(2)
	O(5)	1.93(3)		Cr(2)	2.96(2)
	O(12)	1.97(3)		Cr(3)	3.09(2)
	O(3)	2.08(3)		Cr(2)	3.17(2)
	O(10)	2.22(3)		Cr(1)	3.227(7)
O(1) --	B(4)	1.36(4)			
	B(6)	1.77(3)			
	B(7)	1.91(4)			
	B(5)	2.10(4)			
O(2) --	B(4)	1.36(4)	O(8) --	B(1)	1.38(5)
	B(1)	1.51(4)		B(5)	1.42(4)
O(3) --	B(2)	1.33(5)	O(9) --	B(2)	1.34(5)
	B(4)	1.36(4)		B(7)	1.50(5)
O(4) --	B(6)	1.48(4)	O(10) --	B(6)	1.30(5)
	B(3)	1.81(4)		B(1)	1.31(5)
O(5) --	B(2)	1.64(5)	O(11) --	B(3)	1.48(5)
	B(5)	1.76(4)		B(4)	1.71(4)
O(6) --	B(7)	1.24(4)	O(12) --	B(5)	1.19(5)
	B(3)	1.65(5)		B(1)	1.61(6)
O(7) --	B(2)	1.65(4)	O(13) --	B(7)	1.49(5)
	B(6)	1.67(4)		B(3)	1.49(5)

The positions of boron atoms were refined by fixing all other atoms positions, and then fixed in the final refinement. The residuals (without the contribution of boron atoms) were $R_p = 0.0273$ and $R_B = 0.0723$. The atomic parameters, partially standardized by using the *STRUCTURE TIDY* programme,[9] are listed in Table I. The bond distances as calculated by the BONDLA programme of the XTAL 2.6 system[10] are listed in Table II.

Lattice parameter measurements as a function of temperature were also performed for the tetragonal LT modification on an optically examined single-domain crystal (0.212 × 0.550 × 0.025 mm^3) by using a CAD-4 automatic four-circle diffractometer equipped with a liquid-nitrogen cooling device (model FR 537, Enraf-Nonius, Delft) and a polarizing microscope. The tetragonal domain was stabilized by cycling the crystal across the orthorhombic-to-tetragonal phase transition. Lattice parameters were refined from measured 2θ values of 24 reflections ($2\theta > 76°$) in the temperature interval between 169 K and 298 K. The results are represented in Figures 1 and 2 and compared with those of the cubic and orthorhombic modifications. The structure expands abruptly by about 0.45% at the cubic-to-tetragonal phase transition, whereas no significant volume change occurs at the tetragonal-to-orthorhombic phase transition. The differences between the cell parameters measured by single-crystal and powder diffraction are presumably due to systematic errors.

DISCUSSION

The structure of Cr—Cl at 100 K has all characteristics typical for orthorhombic boracites such as Mg—Cl[7], Cu—Cl[11], Ni—Br[12], Co—Br and Ni—Cl[13]. It contains three independent metal sites, each coordinated by four close oxygens forming a nearly square-planar configuration, and two more distant halogens completing an octahedral-like configuration. One halogen is strongly and the other weakly bonded to the central metal atom. Interestingly, the difference between the two metal-halogen bond-lengths, delta[M-X], in Cr—Cl is much smaller, on the average, than those in the other known orthorhombic boracite structures (delta[M-X]_{av} = 0.26 Å (Cr—Cl), 0.72 Å (Mg—Cl[7]), 0.52 Å (Cu—Cl)[11], 0.71 Å (Ni—Br)[12], 0.65 Å (Co—Br) and 1.03 Å (Ni—Cl)[13]). This is remarkable because Cr—Cl is the only boracite that shows an intermediate tetragonal LT modification in which one metal site has a five-fold coordination (4O + 1Cl) typical of orthorhombic and trigonal LT modifications, and four other metal sites which have a sixfold coordination (4O + 2Cl) typical of the cubic HT modification. The existence of that intermediate phase was interpreted as being due to a tendency of the Cr^{2+} ions to maintain their octahedral environment.[3] The structure data of the orthorhombic Cr—Cl phase support this interpretation. The reason why such a tendency is particularly pronounced in Cr—Cl is unknown, but presumably due to electronic factors. As to the boron-oxygen network no major structural changes occur during the tetragonal-to-orthorhombic phase transition, in contrast to the cubic-to-tetragonal phase transition during which a breaking of boron-oxygen bonds occurs. These observations are consistent with continuous and discontinuous changes of the cell volumes at the tetragonal-to-orthorhombic and cubic-to-tetragonal transition, respectively, with birefringence measurements,[2] and with transition enthalpies[14] which are 60–70 times smaller at the orthorhombic-to-tetragonal transition than at the tetragonal-to-cubic transition.

ACKNOWLEDGEMENT

The authors are grateful to Mr. R. Cros for preparing the figures, and to the Swiss National Science Foundation for financial support.

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