Refinement of the crystal structure of zirconium dodecaboride, ZrB_{12}, *at 140 K and 293 K*

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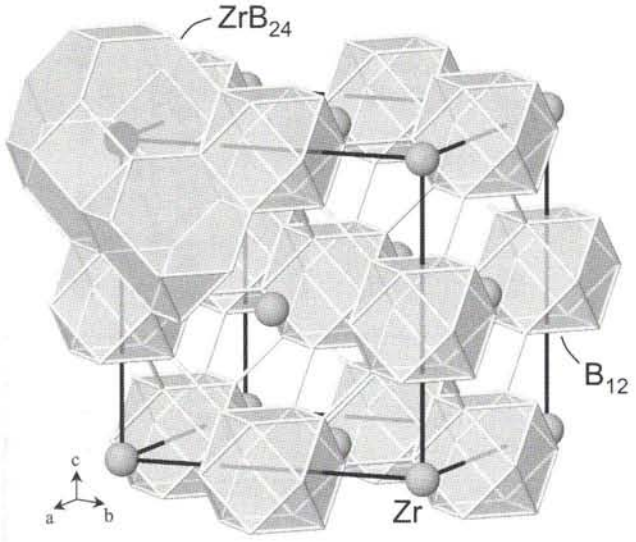

Abstract

$B_{12}Zr$ (1), cubic, $Fm\bar{3}m$ (No. 225), $a = 7.4043(1)$ Å, $V = 405.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.012$, $wR_{ref}(F^2) = 0.031$, $T = 140$ K.

$B_{12}Zr$ (2), cubic, $Fm\bar{3}m$ (No. 225), $a = 7.4075(1)$ Å, $V = 406.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.012$, $wR_{ref}(F^2) = 0.030$, $T = 293$ K.

Source of material

Bulk material was produced by sintering appropriate mixtures of ZrB_2 and B powder (99.9 wt.%) at 2073 K in an inductively heated carbon-free susceptor. Since ZrB_{12} has an incongruent melting behavior (T_m = 2353 K) [1], several starting materials compositions ($ZrB_{15} - ZrB_{19}$) were prepared. Ceramic green bodies were then manufactured containing camphor as lubricant, by isostatic pressing at about 250 MPa in rubber pipes of appropriate diameters. The so formed cylindrical bodies were placed in a carbon free susceptor and subjected to a heat treatment program in a conventional RF-heating furnace under vacuum of about 3×10^{-8} Pa. Slow heating to a level at a moderate temperature enables smooth evaporation of the camphor binder. Subsequent heating to 2073 K and maintaining this temperature for several hours enhances the grain growth and thus favors dense sintering. Crystal growth was performed by floating zone melting in a NEC single mirror-type image furnace. The feed rod and the seed rod (ZrB_{12} seed crystal) were set on the upper and lower axes, respectively. The crystal growth was performed by downward driving of both, the feed rod and the seed rod, synchronously at a rate of 5 mm/h. Both rods were counter-rotated at 40 rpm and the atmosphere was flowing argon. Despite the eutectoid decomposition (T= 1963 K) reported for ZrB_{12} [1], large high quality single crystals were grown for the first time. Chemical analysis of the crystals gave a composition of $Zr_{0.98(2)}B_{12}$ with carbon and oxygen contamination below 0.06 wt.%.

Experimental details

Refinement of the room temperature data set resulted in a large extinction coefficient (0.167952). Cooling the crystal to 140 K by a N_2 cryo stream enabled a refinement with a smaller extinction (0.099440) coefficient.

Discussion

ZrB_{12} adopts the UB_{12} [2-4] type of structure. The boron atoms form one type of B_{12} cuboctahedral unit. The interconnection of the cuboctahedra gives rise to large truncated octahedra which are centered by Zr atoms and truncated tetrahedra. The bond lengths between boron atoms are observed in the range of 1.68 Å < d_{BB} < 1.78 Å. The shorter is a inter-cuboctahedral one and the longer is a intra-cuboctahedral one.

1. Zirconium dodecaboride, ZrB_{12}, at 140 K

Table 1. Data collection and handling.

Crystal:	silver grey parallelepiped, size 0.12 × 0.10 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	25.12 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, ω
$2\theta_{max}$:	89.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	494, 118
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 118
$N(param)_{refined}$:	7
Programs:	SHELX-97 [5], ATOMS [6]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	4*a*	0	0	0	0.0038(1)	U_{11}	U_{11}	0	0	0
B	48*i*	1/2	0.66982(7)	y	0.0041(2)	0.0046(2)	U_{22}	0	0	–0.0007(2)

2. Zirconium dodecaboride, ZrB_{12}, at 293 K

Table 3. Data collection and handling.

Crystal:	silver grey parallelepiped, size 0.12 × 0.10 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	25.09 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, ω
$2\theta_{max}$:	89.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	494, 118
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 118
$N(param)_{refined}$:	7
Programs:	SHELXL-97 [5], ATOMS [6]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	4*a*	0	0	0	0.0057(1)	U_{11}	U_{22}	0	0	0
B	48*i*	1/2	0.66981(6)	y	0.0044(2)	0.0054(2)	U_{11}	0	0	–0.0011(1)

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