

# Crystal structure of the $\text{GdCo}_2\text{B}_2\text{C}_x$ ( $x=0-1$ )

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**Abstract:**  $\text{GdCo}_2\text{B}_2\text{C}_x$  ( $x=0-1$ ) has been synthesized to study the role of C in the formation of new quaternary compounds  $\text{RT}_2\text{B}_2\text{C}$  (R = rare earth, T = transition metal);  $\text{RT}_2\text{B}_2\text{C}$  belongs to a tetragonal system with  $\text{ThCr}_2\text{Si}_2$  derivative type. Samples of  $\text{GdCo}_2\text{B}_2\text{C}_x$  ( $x=0, 0.25, 0.50, 0.75$  and  $1.00$ ) were prepared by the arc-melting synthetic method. The lattice parameter  $a$  slightly decreased, while the lattice parameter  $c$  and the unit cell volume increased with increasing  $x$  in  $\text{GdCo}_2\text{B}_2\text{C}_x$ . This result shows that C element serves to expand the entire unit cell in the shape of a square column composed of R atoms (eight at the corners) especially along the  $c$ -direction, and permit T atoms, which are too large for the normal lattice, to join in combination. The role of C to form the quaternary borocarbides  $\text{RT}_2\text{B}_2\text{C}$  has been discussed.

**Keywords:**  $\text{GdCo}_2\text{B}_2\text{C}_x$  ( $x=0-1$ ), Quaternary borocarbides, Crystal structure

## 1. Introduction

The crystal chemistry of R-T-B and R-T-B-C (R = rare earth element, T = transition element) systems has received considerable attention from many researchers in the fields of crystallography, magnetism, superconductivity, heavy-electron behaviour, valence fluctuations and catalytic properties<sup>[1-4]</sup>. To study the crystallographic relationship between two compounds of  $\text{RT}_2\text{B}_2$  (tetragonal system;  $\text{ThCr}_2\text{Si}_2$  type structure) and  $\text{RT}_2\text{B}_2\text{C}$  (tetragonal system; modified model of  $\text{ThCr}_2\text{Si}_2$  type structure), in which a rare-earth element R and a transition element T are specified, is considered important in considering what role is being played by the element C during the formation of the latter borocarbide compound, in particular. However, in case some of these are present, the others are not likely to be present. Within the range of the investigation carried out up to now by the authors, it is only in a combination of  $\text{GdCo}_2\text{B}_2$  and  $\text{GdCo}_2\text{B}_2\text{C}$  that boride and borocarbide are present at the same time. In regard to  $\text{GdCo}_2\text{B}_2$ , a group including one of the present authors reported<sup>[5]</sup>. On the other hand, in respect to  $\text{GdCo}_2\text{B}_2\text{C}_2$ , Mulder et al. have recently given a report<sup>[6]</sup>.

In this study, compounds were prepared by varying the quantity  $x$  of C in  $\text{GdCo}_2\text{B}_2\text{C}_x$  between 0 and 1, and an investigation was carried out into how the crystal structure changes depending on the amount of C.

## 2. Experimental Details

### 2.1 Synthesis of Compounds

For raw materials, 99.9% Gd (block) by Nippon Yttrium, 99.96% cobalt (powder) by Hirano, 99.86% crystalline boron (aggregate) by Hirano, and 99.999% carbon (block) by Kojundo Kagaku Kenkyusho were used. The blocks were cut into small pieces, while the aggregate was pulverized and made into powder. An attempt was made to synthesize compounds by an arc melting method. Compounds were synthesized by varying the amount of  $x$  in  $\text{GdCo}_2\text{B}_2\text{C}_x$  continuously. In other words, the raw materials were mixed so as to have an atomic ratio of Gd : Co : B : C = 1 : 2 : 2 : 0, 1 : 2 : 2 : 0.25, 1 : 2 : 2 : 0.50, 1 : 2 : 2 : 0.75, and 1 : 2 : 2 : 1.00. A total of about 2.5 g of the raw materials were placed inside a copper health, and the vacuum level inside the chamber was reduced to about  $7 \times 10^{-3}$  N/m<sup>2</sup>. Then argon gas was injected in the oven to a pressure of 1 atm. By generating an argon arc plasma flame, titanium for the oxygen getter was first heated and melted to remove traces of oxygen remaining inside the chamber. Next, by focusing the flame on the raw materials, they were melted for 3 min with AC 20 V  $\times$  100 A to cause reactions. The samples were then turned over and melted three times under the same conditions.

### 2.2 Analysis

The chemical compositions of the three elements Gd, Co, and B were investigated by using an inductively coupled plasma atomic emission spectrometry (ICP-AES). The samples were dissolved in a mixed acid of nitric acid, hydrochloric acid, and phosphoric acid, and were measured by the ICP method. The element C was measured by a combustion-infrared absorption method. Substances obtained by adding high-purity Fe, W and Sn to the samples were placed inside a mortar and were heated at a high-frequency wave while flowing oxygen. Fe, W and Sn acted first as activators for introducing the high-frequency wave

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into the contents of the mortar, and then worked as solvent (fluxing agent) for the samples after the entire contents had been heated to a high temperature. C inside the samples is burned to become  $\text{CO}_2$ , which is then transported by oxygen.  $\text{CO}_2$  was measured by an infrared absorption method. By determining the entire amount of  $\text{CO}_2$  by integration and converting this into the amount of C, this amount was assumed to be the amount of C in the original samples. The identification of the compounds and the determination of the lattice constants were carried out by a powder XRD method using copper as its beam source. By profile-fitting the 20 values of the peaks, the lattice constants were measured.

### 3. Results and Discussion

#### 3.1 Chemical Compositions

The ingot obtained by completing the arc-melting synthesis has a silvery luster. The results of the chemical analyses are listed in Table 1. A comparison of the chemical compositions of the samples after the synthesis with the starting compositions indicates that Gd is shifted slightly to the larger-value side and B to the smaller-value side, while Co and C are stationary.

#### 3.2 Crystal Structure of Compounds

Fig. 1 presents the XRD profiles of the samples obtained. The compositions of  $x=0, 0.25, 0.50, 0.75$  and  $1.00$  in  $\text{GdCo}_2\text{B}_2\text{C}_x$  correspond to the profiles (a) through (e), respectively. Each spot with a circle (○) indicated a tetragonal system compound. In terms of their correspondence with the concentration  $x$  of C, it is suggested that as  $x$  increases from  $x=0$ , the group of peaks with ○ shifts relatively toward the lower-angle side and the unit lattice volume increases gradually. Throughout the entire synthesized samples the main impurity phase is the  $\text{GdCo}_3\text{B}_2$  phase indicated by ▽ in the profile. The  $\text{GdCo}_3\text{B}_2$  phase gradually decreases as the concentration of C increases. The crystal structures of the two compounds are illustrated in Fig. 2(a) and (b). Boride  $\text{GdCo}_2\text{B}_2$  is a tetragonal system compound of the  $\text{ThCr}_2\text{Si}_2$  type. On the other hand, borocarbon  $\text{GdCo}_2\text{B}_2\text{C}$  is a modified model based

on the  $\text{ThCr}_2\text{Si}_2$  type, and is a more complex compound to the extent of containing C. Each of these has the element Gd occupying the eight corner positions of the frame. An investigation was carried out into the relationship between the contraction of C and lattice constants. With an increase in the level of the C content as indicated in Fig. 3 (a), the value of the lattice constant  $a$  lowers (even though no change occurs monotonously). However, a comparison of the difference in C amount between  $x=0$  and  $x=1$  indicates that the change in the lattice constant  $a$  is as extremely small as  $0.003$  nm. The element C is introduced to the base center of Fig. 2(b), but depending on the amount introduced, the  $a$ -axis is considered to contract as the interface bond between the rare-earth element Gd and C gets stronger. This situation is illustrated by horizontal

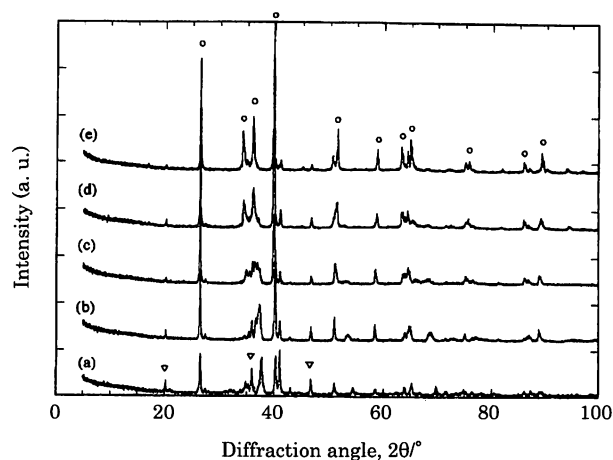


Fig. 1 XRD profiles of  $\text{GdCo}_2\text{B}_2\text{C}_x$  (○) with  $x=0$  (a),  $0.25$  (b),  $0.50$  (c),  $0.75$  (d) and  $1.00$  (e). Peaks from impurity phase of  $\text{GdCo}_3\text{B}_2$  (▽) are also indicated.

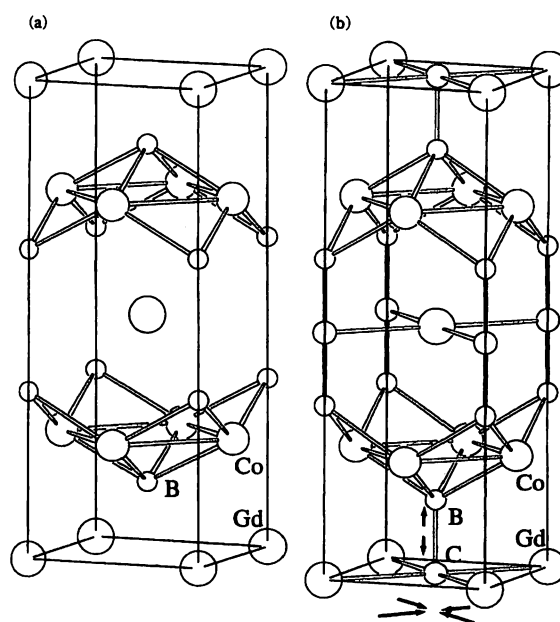
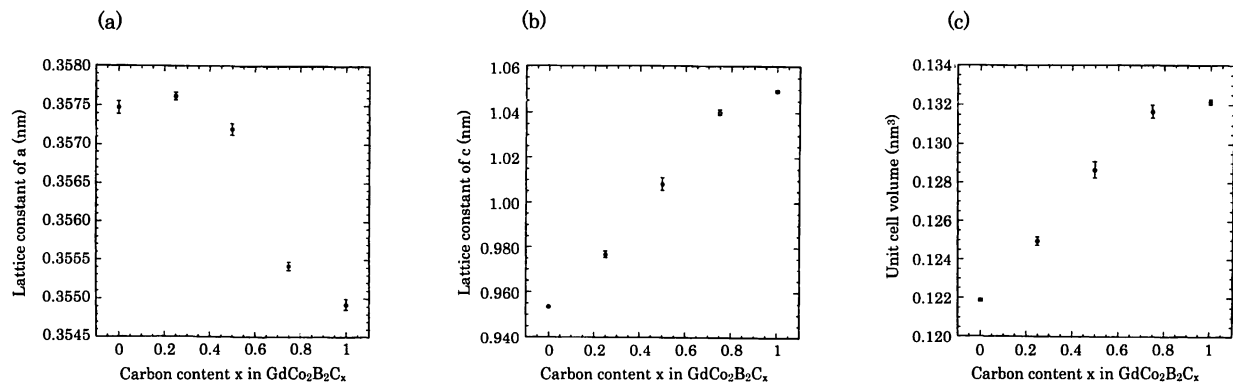


Fig. 2 Crystal structure of  $\text{GdCo}_2\text{B}_2$  (a) and  $\text{GdCo}_2\text{B}_2\text{C}$  (b).

Table 1 Results of the chemical analyses on the synthesized samples for the  $\text{GdCo}_2\text{B}_2$ – $\text{GdCo}_2\text{B}_2\text{C}$  system

Nominal composition	Results of the chemical analyses mass% (Nominal composition)			
	Gd	Co	B	C
$\text{GdCo}_2\text{B}_2\text{C}_{0.00}$	54.1 (52.99)	39.7 (39.72)	5.62 (7.29)	(0.00)
$\text{GdCo}_2\text{B}_2\text{C}_{0.25}$	53.4 (52.46)	39.2 (39.32)	6.25 (7.21)	0.99 (1.00)
$\text{GdCo}_2\text{B}_2\text{C}_{0.50}$	52.3 (51.94)	38.6 (38.93)	6.34 (7.14)	2.00 (1.99)
$\text{GdCo}_2\text{B}_2\text{C}_{0.75}$	52.0 (51.43)	38.2 (38.55)	6.22 (7.07)	2.93 (2.95)
$\text{GdCo}_2\text{B}_2\text{C}_{1.00}$	52.0 (50.93)	38.1 (38.17)	6.13 (7.00)	3.59 (3.89)



**Fig. 3** The lattice constant  $a$  (a), lattice constant  $c$  (b) and unit cell volume (c) as a function of the carbon content  $x$  in  $\text{GdCo}_2\text{B}_2\text{C}_x$ .

arrows in Fig. 3(b). On the other hand, if the C content in the compound increases as indicated in Fig. 3(b), then the value of the lattice constant  $c$  increases almost linearly. In this case, a comparison of the difference in the C content between  $x=0$  and  $x=1$  shows that the change in the lattice constant  $c$  is extremely large at 0.10 nm. A possibility is considered to exist that a repulsive force works on the bond between C, introduced to the bottom center of Fig. 3(b), and B that already exists right above it. A strong bond exists between C and Gd or between B and Co; it is therefore considered that in proportion to an increase in the amount of C introduced, repulsion to the bond between C and B takes place, thereby causing the frame to expand considerably in a vertical direction. This situation is indicated by vertical arrows in Fig. 3(b). The size of the unit cell volume as a whole body increases almost linearly with an increase in the C content, as indicated in Fig. 3(c). A comparison in C content between  $x=0$  and  $x=1$  indicated that the unit cell volume in the latter increases by about 8.5%. Nevertheless, the vacant areas inside the lattice for the latter are also considered to increase, so the volume decreases by 4.3% on the contrary, in accordance with a comparison in X-ray density. Table 2 presents crystallographic data on  $\text{GdCo}_2\text{B}_2$  and  $\text{GdCo}_2\text{B}_2\text{C}$ . The lattice constants of  $\text{GdCo}_2\text{B}_2$  are  $a=0.35747(8)$  nm and  $c=0.9537(2)$  nm. The crystal structure of  $\text{GdCo}_2\text{B}_2\text{C}$  is basically the same as those of  $\text{GdRh}_2\text{B}_2\text{C}$  and  $\text{ErRh}_2\text{B}_2\text{C}$ , on which the authors have reported previously. Here, if a comparison is made between the values of the lattice constants obtained by the authors and by Mulder et al., then  $a=0.35492(7)$  nm and  $c=1.0491(5)$  nm vs.  $a=0.3548$  nm and  $c=1.0271$  nm.

The results of the present experiment may be regarded as providing a suggestion in considering the role of the element C in the formation of 4f-element system borocarbide  $\text{RT}_2\text{B}_2\text{C}$ <sup>[7-16]</sup>.

#### 4. Conclusion

By synthesizing compounds by arc melting while changing the amount of C continuously to set  $x=0, 0.25, 0.50, 0.75$  and  $1.00$  in  $\text{GdCo}_2\text{B}_2\text{C}_x$ , an investigation was con-

**Table 2** Crystallographic data of the  $\text{GdCo}_2\text{B}_2$  and  $\text{GdCo}_2\text{B}_2\text{C}$ .

Chemical formula	$\text{GdCo}_2\text{B}_2$	$\text{GdCo}_2\text{B}_2\text{C}$
Crystal system	Tetragonal	Tetragonal
Structure type	$\text{ThCr}_2\text{Si}_2$ type	derivative of $\text{ThCr}_2\text{Si}_2$ type
Number of molecules per unit cell Z	2	2
Lattice parameter		
$a$ (nm)	0.35747 (8)	0.35492 (7)
$c$ (nm)	0.9537 (2)	1.0491 (5)
Unit cell volume, V ( $\times 10^{-28}$ m <sup>3</sup> )	1.2187(8)	1.322(1)
X-ray density, g/cm <sup>3</sup>	8.09	7.76

ducted into how the structures and lattice constants of the samples changed. The chemical compositions of the samples after the synthesis shift slightly, relative to the compositions of the raw materials, toward the larger-value side in the case of Gd and toward the smaller-value side for B, but no shift is seen in the case of Co and C. According to the results of a powder XRD analysis, with an increase in the amount of C, the value of the lattice constant  $a$  declines somewhat, the value of the lattice constant  $c$  increases considerably, and the unit cell volume increases greatly. It is thought that the lattice constant  $a$  contracts slightly because it is subjected to a strong bond between C, introduced into the base center of the tetragonal crystal system, and Gd, which receives it, and that the lattice constant  $c$  expanded greatly as a repulsion to the bond between C and B present right above it due to the introduction of C.

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### References

- [ 1 ] L. D. Woolf, D. C. Johnston, H. B. MacKay, R. W. McCallum, M. B. Maple, J. Low Temp. Phys., 35, 651 (1979).
- [ 2 ] B. K. Cho, M. Xu, P. C. Canfield, L. L. Miller, D. C. Johnston, Phys. Rev., B52, 3767–3772 (1995).
- [ 3 ] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature, 410, 63–66 (2001).
- [ 4 ] T. Shishido, J. Ye, K. Kudou, S. Okada, K. Iizumi et al., J. Alloys Compds., 375, 217–220 (2004).
- [ 5 ] K. Niihara, T. Shishido and S. Yajima, Bull. Chem. Soc. Jpn., 46, 1137–1140 (1973).
- [ 6 ] F. M. Mulder, J. H. V. J. Brabers, R. Coehoorn, R. C. Thiel, K. H. J. Buschow and F. R. de Boer, J. Alloys Compounds, 217, 118–122 (1995).
- [ 7 ] C. Mazumundar, R. Nagarajan, C. Godarat, L. G. Gupta, M. Latroche, S. K. Dhar, C. Levy-Clement, B. D. Padalia and R. Vijayaraghavan, Solid State Commun., 87, 413–416 (1993).
- [ 8 ] R. J. Cava, H. Takagi, B. Batlogg, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, Jr., R. B. van Dover, R. J. Felder, T. Siegrist, K. Mizuhashi, J. O. Lee, H. Eisaki, S. A. Canter and S. Uchida, Nature, 367, 146–148 (1994).
- [ 9 ] R. J. Cava, H. Takagi, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, Jr., T. Siegrist, B. Batlogg, R. B. van Dover, R. J. Felder, K. Mizuhashi, J. O. Lee, H. Eisaki and S. Uchida, Nature, 367, 252–253 (1994).
- [ 10 ] R. Nagarajan, C. Mazumundar, Z. Hossain, S. K. Dhar, K. V. Golpakrishnan, L. C. Gupta, C. Godart, B. D. Padalia and R. Vijayaraghavan, Phys., Rev. Lett., 72, 274–277 (1994).
- [ 11 ] T. Shishido, J. Ye, T. Sasaki, T. Matsumoto and T. Fukuda, J. Ceram. Soc. Jpn., 104, 1117–1120 (1996).
- [ 12 ] J. Ye, T. Shishido, T. Matsumoto and T. Fukuda, Acta Cryst. C, 54, 1211–1214 (1998).
- [ 13 ] J. Ye, T. Shishido, T. Matsumoto and T. Fukuda, Acta Cryst. C, 52, 2652–2655 (1996).
- [ 14 ] T. Shishido, J. Ye, T. Sasaki, R. Note, K. Obara, T. Takahashi, T. Matsumoto and T. Fukuda, J. Solid State Chem., 133, 82–87 (1997).
- [ 15 ] J. Ye, T. Shishido, T. Sasaki, T. Takahashi, K. Obara, R. Note, T. Matsumoto and T. Fukuda, J. Solid State Chem., 133, 77–81 (1997).
- [ 16 ] T. Shishido, J. Ye, K. Obara and T. Fukuda, J. Ceram. Soc. Jpn., Int. Edition, 106, 310–313 (1998).