Revised Structure of the Orthoborate YBO₃

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The YBO₃ orthoborate was prepared by a flux evaporation process and the diffraction lines of its X-ray pattern were indexed on the basis of single crystal data. Crystal structure was determined ($R = 0.035$) in the $P6_3/m$ space group from data recorded on a four-circle automatic diffractometer, with cell parameters $a = 3.776$ (1) Å, $c = 8.806$ (4) Å. The structure consists of a three-dimensional network made up of eightfold coordinated yttrium atoms and fourfold coordinated boron atoms. The structure exhibits two nonequivalent environments for the yttrium ions, which is confirmed by luminescence studies using the Eu^{3+} ion as structural probe. This work was completed by ^{11}B NMR and IR studies, which show that boron has tetrahedral coordination. © 1997 Academic Press

1. INTRODUCTION

During the past few years, much interest has been devoted to the study of yttrium and lanthanide orthoborates because of their high UV transparency and exceptional optical damage threshold, which make them attractive for numerous practical applications.

Nevertheless, the large number of studies concerning the rare earth orthoborates LnBO₃ have not always clearly identified their crystallographic structures.

In 1961, Levin *et al.* (1) investigated their polymorphism and reported on the regions of stability of the different structures in relation with borates preparation temperature and the ionic radius of the rare earth. The diagram they established showed that the structures of the rare earth borates are related to the three crystalline forms of CaCO₃, aragonite, vaterite, and calcite, depending on the rare earth.

The compounds LaBO₃, NdBO₃ (1), and CeBO₃ (2) exhibit the aragonite-type structure up to 1450, 1300, 1500°C, respectively, and crystallize in the orthorhombic system with space group *Pnam* ($Z = 4$). A recent study of the luminescence of Eu^{3+} in NdBO₃ (3) confirms these results

and proposes a C_s symmetry site for the rare earth. At higher temperatures, two different forms (denoted H) have been found for LaBO₃ and NdBO₃. According to Bohlhoff *et al.* (4), they crystallize in the monoclinic system. Moreover, we have pointed out that these H-forms also exist at low temperature (about 600°C) when the compounds are prepared by the sol–gel technique.

For the smallest rare earth ions (Sm to Lu) the orthoborates possess the vaterite structure, which is consistent with a pseudo-hexagonal symmetry. In this series, SmBO₃ and EuBO₃ present both vaterite and H-forms. However, there remains some ambiguity. For YBO₃, Newnham *et al.* (5) proposed two space groups, a disordered hexagonal $P6_3/mmc$ with only one D_{3d} point symmetry for the rare earth, and an ordered hexagonal $P6_3/mcm$, with two kinds of point symmetry sites for the rare earth (D_3 and D_{3d}). Then Bradley (6) confirmed the D_3 point symmetry for the rare earth but using the $P\bar{6}c2$ space group. Despite the uncertainty about the crystal structure of YBO₃, several studies using IR, NMR, and Raman data pointed out that the boron atoms form a B_3O_9 unit with tetrahedral coordination (7–9). Recently, Hölsä (10), studying the luminescence of Eu^{3+} as a structural probe in LuBO₃, proposed for the vaterite type two kinds of sites for Lu, with D_{3d} and T point symmetries.

In the third series of borates, InBO₃, LuBO₃, and ScBO₃ (1, 11–13) are known to exhibit the calcite type structure. Let us note that LuBO₃ presents both a low-temperature calcite form and a high-temperature vaterite form. The calcite structure has a rhombohedral symmetry. The space group is $R\bar{3}c$ ($Z = 6$) with a single site for the rare earth having S_6 point symmetry.

For the vaterite structure which is our aim the luminescence results given in the literature lead to two kinds of sites, D_{3d} and T, for the rare earth, as mentioned before (10). Our optical studies on YBO₃:Eu^{3+} have led to two intrinsic sites of C_3 symmetry (14). These data are not consistent with the crystallographic results (10, 14). Because of these inconsistencies, in this paper, we report the revised crystal structure of YBO₃ determined from X-ray single crystal data. This structure is compared with that of InBO₃.

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EXPERIMENTAL

Synthesis

Powder sample of YBO_3 was prepared by heating in air a mixture of the reagents Y_2O_3 (Rhône Poulenc 99.99%) and H_3BO_3 (Prolabo 99%) in the ratio $Y/B = 1.2$. The mixture was heated in a Pt crucible at 500°C for 2 hr, ground, and again heated at 1100°C for 2 hr. The flux evaporation process using $LiBO_2$ (Strem Chemicals 99.9%) at a solvent has been used for the synthesis of single crystals of YBO_3. The procedure was as follows (11):

YBO_3 (25% wt) and $LiBO_2$ (75% wt) were intimately mixed together on a vibrating machine and then put into a platinum crucible with a closely fitting lid limiting vaporization of the solvent. The crystal growth was carried out in a furnace, the temperature of which was regulated and programmed by a 9 P Eurotherm controller. After the crucible was introduced into the furnace, the thermal program was initiated. The starting materials were heated up to 1150°C at a rate of 100°C/h then maintained for 10 hr at this temperature and cooled to 840°C at a rate of 3°C/h and finally to room temperature at a rate of 100°C/h. Owing to the acidic character of YBO_3, a basic flux is required for dissolution and growth (15). $LiBO_2$ was chosen both for its basic properties and for its low melting point. After washing with hot distilled water $LiBO_2$ was dissolved and crystals were obtained.

Structure Determination

A colorless crystal was selected from the synthesized specimen. Unit cell dimensions were determined accurately using a four-circle Nonius CAD4 diffractometer by centering on 25 reflections with $14 \leq 2\theta \leq 40$ and least-squares refinement of the measured setting angles. Data collection parameters are given in Table 1.

At first, the superstructure with $a' = a\sqrt{3}$ proposed by Bradley does not prove necessary to index the X-ray diffraction pattern. Moreover, further refinements were not successful.

The crystal structure of YBO_3 was solved in the $P6_3/m$ space group (No. 176) with the program MolEN (16), the atomic scattering and anomalous dispersion factors for atoms being taken from the International Tables for X-Ray Crystallography (17). The refinement converged to $R = 0.035$ after introduction of anisotropic temperature factors except for boron atom; a secondary extinction correction improved the refinement. Atomic coordinates with isotropic thermal parameters are listed in Table 2, anisotropic displacement parameters in Table 3, and significant interatomic distances and angles in Table 4.

The powder X-ray diffraction patterns are indexed with cell parameters $a = 3.772$ Å, $c = 8.791$ Å, which are in agreement with the single crystal results (Table 1). The observed and calculated d spacings and the associated relative intensities of the powder X-ray diffraction reflections are listed in Table 5.

Let us mention that comparison between theoretical X-ray diffraction pattern ($P6_3/m$ space group) and observed X-ray diffraction pattern of YBO_3 provides evidence for the new crystallographic results which it is not the case for the assumption of Bradley.

TABLE 1
Crystal Data and Details of the X-Ray Data Collection of YBO_3

Chemical formula	YBO_3
Formula weight	147.71
Space group	$P6_3/m$ (No. 176)
Cell dimensions	$a = 3.776(1)$ Å
	$c = 8.806(4)$ Å
Z	2
Density (calculated)	2.26 g/cm^3
Linear absorption coefficient	133.4 cm^{-1}
Crystal size (mm)	$0.03 \times 0.18 \times 0.35$
Radiation	$MoK\alpha(0.71073)$ Å
	graphite monochromated
Temperature	293 K
Scan:	
mode	ω–2θ
width	$(0.8 + 0.35 \tan\theta)°$
aperture	$(2.7 + 0.4 \tan\theta)$ mm
absorption correction	empirical DIFABS [22]
T_{min}/T_{max}	0.82/1.15
Data collected	$0 \leq \theta \leq 45$
	$0 \leq h \leq 7$
	$0 \leq k \leq 7$
	$0 \leq l \leq 17$
Measured reflections	324
Independent reflections ($I > 3\sigma(I)$)	182
Number of refined parameters	16
Extinction coefficient	2.138×10^{-6}
Weighting scheme	unit
Final Fourier residuals	1.67 e Å^{-3}, and -1.12 e Å^{-3}
Final R indices ($I > 3\sigma(I)$)/S	(0.035–0.041)/1.066
R indices (all data)	0.080–0.077

TABLE 2
Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for YBO_3

Atoms	Wyckoff position	Sites occupancy	x	y	z	B_{eq} (Å^2)^a
Y	2 (b)	1	0	0	0	0.273(6)
O(1)	4 (f)	1	0.667	0.333	0.1103(7)	1.05(6)
O(2)	6 (h)	1/3	0.774(4)	$-0.119(4)$	0.25	0.5(2)
B	6 (h)	1/3	0.586(5)	0.435(5)	0.25	0.4(2)^b

^{a} $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

^{b} Atom refined isotropically.

TABLE 3
General Displacement Parameters

	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)
Y	0.41(1)	0.41(1)	0.00(1)	0.41(1)	0	0
O(1)	1.2(1)	1.2(1)	0.7(2)	1.2(1)	0	0
O(2)	0.4(3)	0.2(2)	0.7(3)	− 0.1(2)	0	0

Eu³⁺ doped orthoborate single crystals have been prepared in the same way as described before by replacing molar proportion of Y_2O_3 by Eu_2O_3 (Rhône-Poulenc 99.99%). In all cases, the structure refinement shows that these compounds are isostructural with YBO_3.

DESCRIPTION OF THE STRUCTURE

Figure 1 represents the projection of YBO_3 unit cell content onto the (001) plane. Y is eightfold coordinated by oxygen atoms in an arrangement which can be described as a trigonal bicapped antiprism. These oxygen surrounding the Y^{3+} ions occupy two positions in the cell: six O(1) atoms in 4 (f) and two O(2) atoms in 6 (h) with a partial occupancy (1/3). The Y–O(1) and Y–O(2) distances are respectively 2.39 and 2.32 Å. Yttrium environments are presented in Fig. 2. Other distributions of O(2) in 6 (h) sites are not possible for steric reasons.

Boron is fourfold coordinated; $[BO_4]$ tetrahedra are in two forms, the first one (I) very regular with B–O distances ranging from 1.37 to 1.57 Å and the second one (II) with two similar bonds (1.37 Å) and two larger ones between 1.89 and 1.92 Å. $[YO_8]$ polyhedra share edges O(1)–O(1) and O(2) corners with two other $[YO_8]$ polyhedra. A view of the crystal structure of YBO_3 along c axis is shown in Fig. 3a. The structure can be described as a 3D unit by $[YO_8]$

TABLE 4
### Selected Interatomic Distances and Angles for YBO₃

Y environment					
Y–O(1)	2.386 (2) × 6	O(1)–Y–O(1)	75.4 (1)	O(1)–Y–O(1)	180.0 (1)
Y–O(2)	2.323 (4) × 2	O(2)–Y–O(2)	180.0 (1)	O(2)–Y–O(2)	147.9 (4)
⟨Y–O⟩ 2.37		O(1)–Y–O(2)	58.4 (4)	O(1)–Y–O(2)	84.6 (3)
		O(1)–Y–O(2)	57.4 (3)		

B environment					
I		**II**			
B–O(1)	1.37 (1) × 2	B–O(1)	1.37 (1) × 2	O(1)–B–O(1)	128.0 (2)
B–O(2)	1.47 (2) × 1	B–O(2)	1.92 (1) × 1	O(1)–B–O(2)	105.9 (6)
B–O(2)	1.57 (1) × 1	B–O(2)	1.89 (1) × 1	O(1)–B–O(2)	111.0 (2)
⟨B–O⟩ 1.44		⟨B–O⟩ 1.64		O(1)–B–O(2)	102.8 (7)

TABLE 5
X-Ray Powder Pattern of YBO₃

d_{exp} (Å)	d_{calc} (Å)	h	k	l	I/I_0
4.4153	4.3956	0	0	2	64.6
3.2752	3.2668	1	0	0	100
3.0710	3.0622	1	0	1	13.7
2.6283	2.6220	1	0	2	83.0
2.2017	2.1978	0	0	4	12.0
2.1843	2.1814	1	0	3	4.6
1.8896	1.8861	1	1	0	33.7
1.8268	1.8235	1	0	4	36.5
1.7364	1.7333	1	1	2	23.6
1.6325	1.6334	2	0	0	7.6
1.6090	1.6059	2	0	1	2.1
1.5333	1.5311	2	0	2	11.6
1.4678	1.4652	0	0	6	1.8
1.4312	1.4313	1	1	4	5.1
1.3384	1.3369	1	0	6	7.5
1.3134	1.3110	2	0	4	6.4
1.2364	1.2347	2	1	0	4.4
1.1899	1.1887	2	1	2	8.1
1.1574	1.1571	1	1	6	2.6

polyhedra, in which each $[BO_4]$ group is connected with two adjacent $[BO_4]$ groups by O(2) atoms and with two adjacent $[YO_8]$ groups by O(1) atoms. The projection of the structure on the [110] orientation of YBO_3 presented in Fig. 3a is compared with $InBO_3$ in the same orientation (Fig. 3b). The geometry of the $[YO_8]$ framework is not similar to that observed for $[InO_6]$ in $InBO_3$ (12). The important difference between the two structures deals with the existence of two more oxygens in the Y polyhedra (6 O(1) and 2 O(2)).

Considering the nature of the Y site in YBO_3, it appears that Y atoms present a unique coordination but two different environments can be observed because of O(2) statistical distribution. Deviation from the ideal local S_6 symmetry is due to the existence of these two O(2) atoms in comparison with the S_6 symmetry observed for In in $InBO_3$.
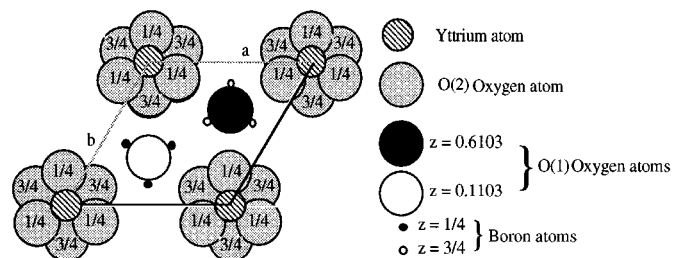
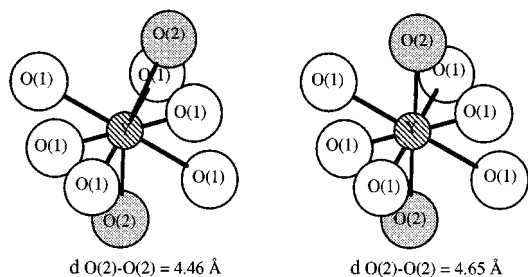**FIG. 1.** Projection of the structure of YBO₃ on the (001) plane.

FIG. 2. Yttrium environment in YBO$_3$.

SPECTROSCOPIC RESULTS

Infrared spectroscopy and ^{11}B nuclear magnetic resonance studies in crystalline borates were carried out in order to specify the coordination of boron atoms.

IR absorption spectra were recorded with a Perkin–Elmer 16 PC spectrophotometer in the 4000–400 cm^{-1} wavenumber range using KBr pellets. Solid state NMR spectra were recorded with a Bruker DSX 400 spectrometer, operating at the ^{11}B resonance frequency of 128,389 MHz with $(C_2H_5)OBF_3$ as external standard. Magical angle spinning technique was used, with a rotation frequency of 12 KHz.

Infra-Red Spectroscopy

Figure 4 shows the spectra of LnBO$_3$ (Ln = La, Y, In) samples prepared by the usual solid state reaction as described previously (14). Vibrations frequencies are listed in Table 6.

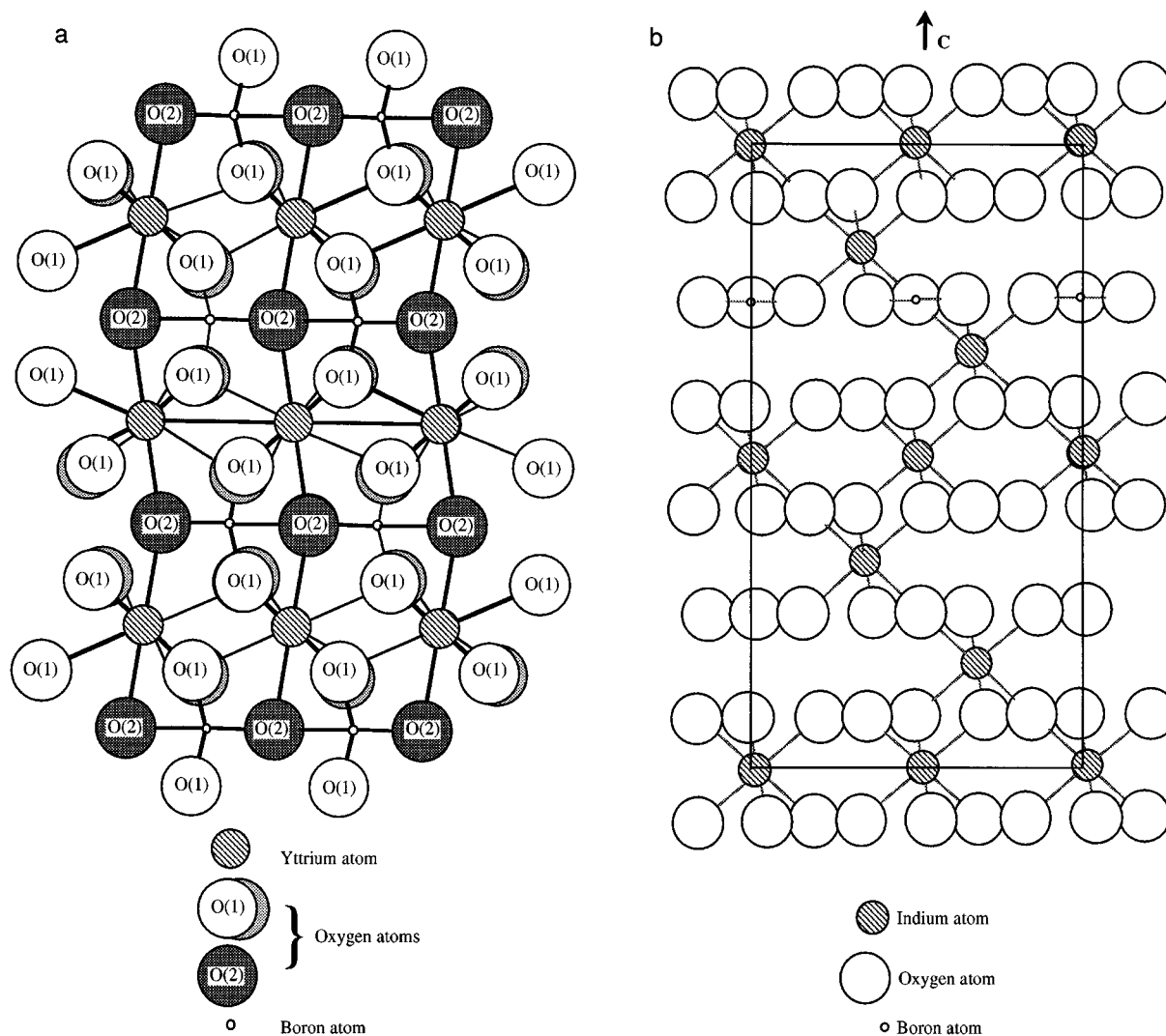In the 1100–850 cm^{-1} range vibrations of B–O groups are certainly observed. For borates with calcite and

FIG. 3. (a) Projection of the structure of YBO$_3$ with a [110] orientation. For the representation O(2) atoms have been arbitrarily placed in the sites corresponding to the second arrangement of Fig. 2. (b) Ball and stick representation of the InBO$_3$ unit cell with a [110] orientation.
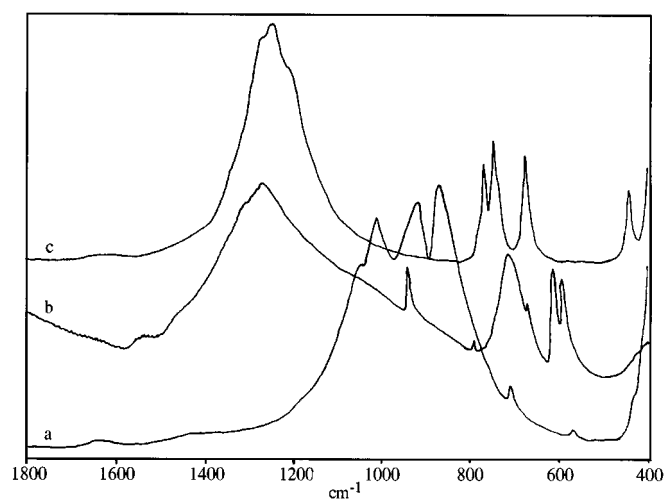
FIG. 4. Infrared spectra of (a) YBO$_3$, (b) LaBO$_3$, and (c) InBO$_3$; prepared by dry method.

aragonite structures (18–19), the boron atoms are threefold coordinated. These results agree with the crystallographic studies. Both aragonite and calcite type borates have vibration modes as follows: v_3 (asymmetric stretching) near

TABLE 6
Observed Frequencies of the Different Vibration Modes in the YBO$_3$, LaBO$_3$, and InBO$_3$ Phases

InBO$_3$ (v cm^{-1}) (calcite)	LaBO$_3$ (v cm^{-1}) (aragonite)	YBO$_3$ (v cm^{-1}) (pseudo-vatérite)
	1541	
	1272 v_3	
1269 v_3		
1245 v_3		
1205 v_3		
	1089 v_3	
		1051
		1011
	938 v_1	
		919
		871
		844
	793 v_2	
764 v_2		
740 v_2		
	712 v_2	
671 v_4		709
	607 v_4	
	585 v_4	
		569
	529	
440		

1300 cm^{-1}, v_2 (out-of-plane bending) near 740 cm^{-1}, and v_4 (in plane bending) in the 670–500 cm^{-1} region. Furthermore, aragonite type borates, in accordance with the selection rules for C_s site symmetry, present v_1 (symmetric stretching) near 940 cm^{-1}. The frequency of B–O vibrations depends on boron coordination, i.e., tetrahedral or trigonal (7). The stretching frequencies of a coordinated XO_n group decrease as coordination number n increases. Therefore, according to the observed frequencies in this range for YBO$_3$-type phases, a coordination number of 4 for boron is more probable (9).

The spectra of both calcite and aragonite structures present a relatively intense band in the 700–800 cm^{-1} range. This vibration corresponds to the v_2 deformation vibrations of BO$_3$ trigonal groups. This band was not observed in borates having pseudo-vaterite structure. Therefore, these results are in good agreement with the crystallographic study.

NMR

The coordination of boron atoms in boron compounds may be correlated to the nuclear magnetic resonance (NMR) signals arising from boron nuclei. A study of the solid state ^{11}B NMR spectra for YBO$_3$ and LaBO$_3$ has been undertaken in order to distinguish boron atoms in threefold and fourfold coordination and to confirm the conclusion based on X-ray and IR studies.

The NMR of LaBO$_3$:Eu^{3+} spectra are easy to analyze (Fig. 5). The two groups of lines (16.7–6.4 and 10.8–3.4 ppm) observed on the spectrum are characteristic of trigonal borons located in two different environments (20, 21). The small peaks which appear around 47.2, 38.0, and −14.6 ppm for example correspond to rotation bands. The comparison between the YBO$_3$:Eu^{3+} and LaBO$_3$:Eu^{3+}
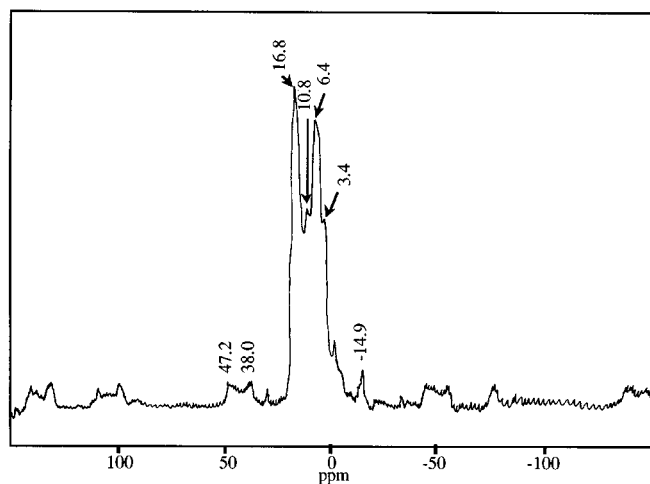

FIG. 5. ^{11}B NMR spectra of LaBO$_3$ prepared by dry method.

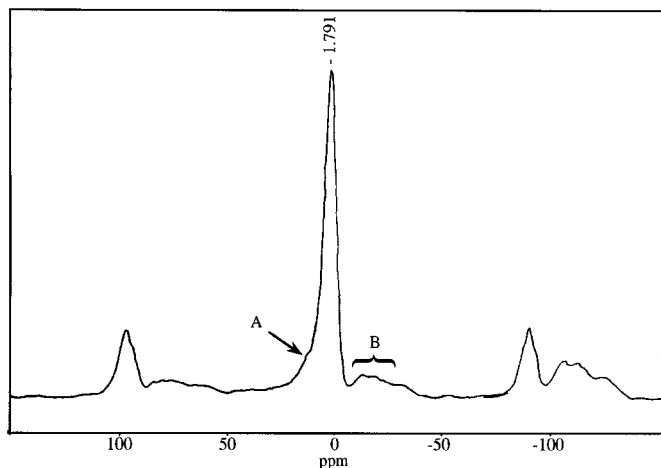**FIG. 6.** ^{11}B NMR spectra of YBO$_3$ prepared by dry method.

spectra shows that boron atoms are differently coordinated. The spectrum of a sample with a 10% Eu^{3+} content is shown on Fig. 6. It is obvious that YBO$_3$ contains mainly BO$_4$ tetrahedra (20). However, the presence of a shoulder (denoted A) on Fig. 6 can be assigned to a different environment for boron which broadens the signal. The B peak could be consistent with boron in threefold coordination but the interpretation of the spectra is difficult in the range from -10 to -50 ppm.

CONCLUSION

This new investigation of the crystal structure of YBO$_3$ determined from X-ray single crystal data shows that yttrium atoms are eightfold coordinated. According to the spectroscopic results, two types of environments for yttrium are observed due to the delocalization of oxygen atoms. The boron atoms are in fourfold coordination with two kinds of anionic environments, one of which is very distorted.

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