On the Presence of (N=B=N)³⁻ Anions in the Structures of Certain Boron Nitrides

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Received May 12, 1998

Abstract — The IR spectra of certain boron nitrides of alkali and alkaline-earth metals, including newly synthesized compounds Ca_6BN_5 , $LiCa_4(BN_2)_3$, $Li_3Mg_3B_2N_5$, Li_3BN_2 , and $Ca_3B_2N_4$ are reported. The spectra confirm the presence of the linear $(N=B=N)^{3-}$ anion in the structures.

Boron nitrides of alkali and alkaline-earth metals are of interest not only as poorly studied new compounds, but also as perspective catalysts–solvents for the transformation of a hexagonal boron nitride (α -BN) to cubic (β -BN) [1–6].

The available information allows such boron nitrides to be characterized as salt-like compounds often colored gray-brown, rather stable thermally, but hydrolyzed in air. A common crystallographic feature of all these compounds is the presence of the quasilinear (N=B=N)^{3–} anion in their structures. The linear structure of BN_2^{3-} is not surprising, as this anion is isoelectronic to the CO_2 molecule [4], and the slight distortion of linearity in the structures of some boron nitrides most probably results from polarization interaction of the anion with cations in the solid state.

Even in early studies of boron nitrides [1] the small number of bands and high frequencies in the IR spectra of boron nitrides (Table 1) were readily accounted for by the presence of such a low-atomic ion with a high bond order as the linear $(N=B=N)^{3-}$ anion. Such anion $(D_{\infty h}$ symmetry) should have three internal vibrations, of which a symmetric stretching vibration (v_1) is active only in Raman spectra, and an asymmetric stretching (v₂) and a doubly degenerate bending vibration (v_3) are active in IR spectra [1, 7]. The bands of boron nitrides between 1637 and 1690 cm⁻¹ (Table 1) belong to the v_2 vibration. The bands at 578 cm⁻¹ observed in the spectrum of $Ca_3B_2N_4$ were assigned [1] to the v_3 vibrations. Rather recently [7] the results of IR studies of the Li₃BN₂, Ba₃B₂N₄, and $Ca_3B_2N_4$ boronitrides were refined and confirmed (Table 2). As expected, all three bands or groups of bands were found in the range $550-1800 \text{ cm}^{-1}$. Of the two IR-active vibrations, v_2 is observed as a doublet due to isotope splitting, whereas v_3 is additionally split because of lifting of degeneracy in the crystal

state and appears as a triplet (Table 2). For all the three boronitrides the intesity ratio $v({}^{10}B)/v({}^{11}B)$ is, as expected, 0.93, which corresponds to the natural content of the ${}^{10}B$ isotope (20%) [7].

As seen from Table 2, there are fairly large in v_1 and v_2 frequencies for diffent cations, on account of the different densities of crystal packings. It is commonly accepted that the packing density increases as the size of the cation decreases, i.e., the free volume available for a single BN_2^{3-} anion should decrease from $Ba_3B_2N_4$ to $Ca_3B_2N_4$. This, in turn, increase intermolecular mutual interaction of the anions, thus providing stronger crowding of the ligands around the central atom [7]. As a result, the force constants of stretching vibrations increase, producing increase in stretching frequencies, first of all, the pulsation frequencies v_1 . This conclusion is confirmed by spectral data (Table 2) which show that v_1 and v_2 fairly strongly vary with the cation, and v_3 remains almost unchanged.

Table 1. Absorption frequencies (cm^{-1}) in the IR spectra of boron nitrides

Ba ₃ B ₂ N ₄ [1]	Li ₃ BN ₂ [1]	Ca ₃ B ₂ N ₄ [1]	Mg ₃ B ₂ N ₄ [3]	Mg ₃ BN ₃ [2]
		295 v.s 395 v.s		
		535 v.s		
		578 m	605	
		703 V.S 915 w	975	
		1145 w		
		1395 w		
1637 s	1662 s	1690 s	1675	
1700 m	1737 m	1760 m		1780

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Fig. 1. IR spectra of (a) Mg_3BN_3 [2] and (b) the new boron nitride Ca_6BN_5 .

The bond orders found from calculated force constants of the $[N=B=N]^{3-}$ anion are 1.9, 1.8, and 2.0 for lithium, barium, and calcium boron nitrides, respectively [7]. For comparison, Table 2 also lists data for K_3BP_2 and K_3BAs_2 [8]; the bond order in the BP_2^{3-} and BAs_2^{3-} anions, isosteric to BN_2^{3-} , is equal to 1.8 and 1.9, respectively.

To confirm qualitatively the presence of BN_2^{3-} anions in the structure of the newly synthesized boronitrides, we first recorded the IR spectra of Ca₆BN₅ (Fig. 1b), $LiCa_4(BN_2)_3$ (Fig. 2), and $Li_3Mg_3B_2N_5$ (Fig. 3a). In this case we did not try to obtain very pure samples and to find the force constants of the anions from the spectral data; therefore, the spectra show bands of admixtures, along with bands of the main substances. However, comparison of the spectrum of Ca_6BN_5 with that of Mg_3BN_3 [2] (Fig. 1), which was used for precise structural calculations, shows that our samples have comparable contents of admixtures (with allowance for instrumental sensitivities). Furthermore, in Figs. 4 and 3b we also give for comparison the spectra of Ca₃B₂N₄ and Li₃BN recorded in the present work.

Some bands, namely the series of bands near 2200 cm⁻¹, the broad band near 3400 cm⁻¹, and also the bands near 820, 920, and 2620 cm⁻¹ were present in the IR spectra of the starting α -BN powders. Taking account of the small number of bands in the IR spectrum of α -BN [9], we assigned these bands to admixtures. As in the synthesis of different boron nitrides we used α -BN of different brands, in the IR



Fig. 2. IR spectrum of the new complex lithium calcium boron nitride $\text{LiCa}_4(\text{BN}_2)_3$.

spectra of the resulting boron nitrides these admixture bands appear as weak bands and series of bands in various combinations. In all other respects the IR spectra of Ca_6BN_5 , $LiCa_4(BN_2)_3$, $Ca_3B_2N_4$, $Li_3Mg_3 \cdot B_2N_5$, and Li_3BN_2 are in a fairly good agreement with the spectrum of Mg_3BN_3 (Fig. 1a) and the spectra presented in Table 2.

Hiraguchi *et al.* [2] assigned the sharp peak with v 3697.5 cm⁻¹ (Fig. 1a) to the OH group of Mg(OH)₂ (resulting from hydrolysis of the admixture of unreacted Mg₃N₂ in air), the broad band near 1450 cm⁻¹ to α -BN, and the band at 1780 cm⁻¹ to the BN₂³⁻ anion, in accordance with the first reported IR spectra of boron nitrides [1]. The refined assignment [7] of the **Table 2.** Frequencies (cm⁻¹) in the vibration spectra of boron derivatives

Vibration	K ₃ BP ₂ [8]	K ₃ BAs ₂ [8]	Li ₃ BN ₂ [7]	Ca ₃ B ₂ N ₄ [7]	Ba ₃ B ₂ N ₄ [7]
$v_1 (\Sigma_g)$	490	274	1057	1107	1028
$v_2(\Sigma_u),$	1131	999	1750	1760	1705
$(\Sigma_u),$	1076	945	1675	1680	1630
(^{11}B)	407	274		()5	(25
$v_3 (\Pi_u),$ (¹⁰ B)	407	3/4	_	625	625
$v_3(\prod_u),$	379	337	575	582	580
(^{11}B)	201	249		607	609
Tatta	391	348	-	607	608 210
Lattice			180	230	219
vibrations			253	284	282
			266		
			367		
			441	400,	
			630		
			650		

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Fig. 3. IR spectra of the boron nitrides (a) $Li_3Mg_3B_2N_5$ and (b) Li_3BN_2 , recorded in this work.

spectra of Li_3BN_2 , $Ca_3B_2N_4$, and $Ba_3B_2N_4$ is given in Table 2. Table 3 lists the assignments of principal bands in the spectra of the first synthesized boron nitrides Ca_6BN_5 [10], $LiCa_4(BN_2)_3$ [11, 12], and $Li_3Mg_3B_2N_5$ [13, 14], we made with account for the above data, and also the spectra of already known $Ca_3B_2N_4$ and Li_3BN_2 in a wider frequency range than in [7].

It should be noted that lattice vibrations of boron nitrides have not been investigated at all, though the vibrations of the boron nitride anion BN_2^{3-} have

Table 3. Assignment of frequencies (cm^{-1}) in the IR spectra of the synthesized boron nitrides

Compound	$ \begin{array}{c} v_2(\Sigma_u), \\ (^{10}\text{B}) \end{array} $	$ \begin{array}{c} \mathbf{v}_2(\boldsymbol{\Sigma}_u), \\ (^{11}\mathbf{B}) \end{array} $	$v_3(\prod_u),$ (¹⁰ B)	$v_3(\prod_u),$ (¹¹ B)	α-BN	OH
Ca ₆ BN ₅	1770 ^a	1700		580 ^b 610 ^b	1384	3640
LiCa ₄ (BN ₂) ₃	1776	1696	650 ^b	592 617 ^a	1384	3648
Li ₃ Mg ₃ B ₂ N ₅	1735	1685	640	615	1490	3670 ^b
Li ₃ BN ₂	1755	1685	630	573 ^a 609 ^b	1375	3675 ^a
Ca ₃ B ₂ N ₄	1756	1684	—	588	1400	3640

^a Very weak bands. ^b Bands observable only at a very slow recording.



Fig. 4. IR spectrum of the boron nitride $Ca_3B_2N_4$, recorded in this work.

been rather well documented. Therefore, part of extraneous bands in the spectra of the new boron nitrides may well relate to their lattice vibrations which, on account of the different symmetry, can very strongly vary in the position and number of bands (as distinct from a rather stable vibrational spectrum of the BN_2^{3-} anion).

Thus, on the basis of published spectral assignments for the BN_2^{3-} anion in various boron nitrides (Tables 1 and 2), we could obtain a rather firm evidence for the presence of the BN_2^{3-} anion in the structures of the new boron nitrides Ca_6BN_5 , $LiCa_4(BN_2)_3$, and $Li_3Mg_3 \cdot$ B_2N_5 , not going into details of their vibration spectra. The IR spectra of $Ca_3B_2N_4$ and Li_3BN_2 taken in this work basically agree with the published spectra of $Ca_3B_2N_4$, Li_3BN_2 [1, 7], and Mg_3BN_3 [2], and all bands in Figs. 4 and 3b have their analogs either in Table 2 or in Figs. 1a, 1b, and 2.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-82 spectrophotometer in KBr and CsI pellets. Therefore, most likely, it is the greater hygroscopicity of KBr compared with CsI, which is responsible for more intense bands in the spectra of Ca_6BN_5 , $LiCa_4(BN_2)_3$, and $Ca_3B_2N_4$, taken in KBr.

The boron nitrides were synthesized as described in [10-14].

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