

Infrared Spectra of the Crystalline Inorganic Borates

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Infrared absorption spectra of anhydrous, crystalline, inorganic borates were obtained in the 2000 cm^{-1} to 300 cm^{-1} range. Compounds with B^{10} and B^{11} isotopes were prepared to assist interpretation. Spectral bands for all orthoborates and pyroborates and some metaborates could be assigned satisfactorily. Borates with complex ring-type anions generally exhibited spectra of such complexity that only superficial interpretation was attempted. From correlations between spectra and structure it appears that boron in 3-fold or in 4-fold coordination can be identified with reasonable assurance on the basis of the infrared spectrum alone. Absorption bands are tabulated for about 80 borates and typical spectra are shown.

1. Introduction

The chemistry of systems containing boron oxide and the structures of glassy and crystalline inorganic borates are of considerable interest in this laboratory. In such work it is evident that the information available from infrared spectroscopy should be of considerable value. Such spectra are easily and rapidly obtained on very small quantities of material and contain direct information on the nature of the borate anion, the coordination of the boron, the strength of the B—O bonds, etc. Although this information is implicit in the absorption spectrum, an explicit derivation of the desired data requires a thorough understanding of the spectrum which is rarely available for any crystalline solid. This work is designed to advance the understanding of the spectra of the crystalline anhydrous borates by recording and correlating the spectrum with the structure of the crystal where this is known. Most structures are unknown so that the data obtained must be interpreted by comparisons, wherever possible, with spectra of crystals whose structure is known.

In addition to the general interest in borates, there is a specific interest here in crystals containing planar trigonal ions. Previous studies on the infrared spectra of carbonates, nitrates, and borates [57]¹ showed many close similarities, but demonstrated a striking difference in the spectra of the borates and the carbonate having the vaterite structure. The reason for the difference was left unresolved. Numerous absorption bands were found in low temperature spectra [48] of single crystals of carbonates and nitrates. These were attributed to combinations of fundamentals and lattice modes. The present survey was considered to be a preliminary requirement to a proposed study of crystals of the borates at low temperatures.

Previous work on the spectra of the borates will not be reviewed in detail here because the majority of such work consists of reports on only one or two

materials. Such references will be discussed in connection with specific spectra. The only comprehensive study of the infrared spectra of anhydrous borates appears to be the recent work of Hart and Smallwood [18]. They studied a large number of borates, but the frequency range used did not extend to sufficiently low frequencies to observe all the fundamental vibrations of interest here. Hart and Smallwood concluded that assignment and interpretation of the more complex spectra was rather difficult. They did not examine several borates for which detailed crystal structures have been reported recently.

In this report, data are tabulated for infrared absorption bands of a number of inorganic borates. In many instances isotopic substitution was employed to assist in the interpretation of the spectra. The data are interpreted in terms of the structure of the anion wherever this is possible.

2. Experimental Method

Infrared spectra were obtained with a double-beam dual-grating spectrometer covering the range 2000 cm^{-1} to 200 cm^{-1} . Higher frequencies were not employed because it was known [18] that fundamentals and most strong overtones and combination bands did not fall above 2000 cm^{-1} in the crystalline compounds. Dry air was circulated through the spectrometer to eliminate interference from atmospheric moisture in the 400 cm^{-1} region. Although the range of the spectrometer extended to 200 cm^{-1} a practical limit of 300 cm^{-1} appeared to be imposed by the available energy.

Spectra were obtained under two conditions, first as a suspension in light petroleum oil, and second as a film produced by evaporation of a CCl_4 suspension. Both KBr and CsBr windows were used with a similar window being placed in the reference beam in all experiments. Mull spectra were used principally in the 1100 cm^{-1} to 300 cm^{-1} region while film spectra were found useful in the region above 1000 cm^{-1} where some interference by absorption in the mineral oil occurred. In the case of film spectra it was fre-

¹ Figures in brackets indicate the literature references at the end of this paper.

quently found useful to expand the absorption peaks along the intensity axis, a similar expansion for the suspension was not possible because of the undesirable magnification of weak absorption bands in the oil. In the region where the two spectra overlapped the positions of absorption bands frequently showed discrepancies of at most 2 cm^{-1} . Under these circumstances the mull spectra were assumed to be correct and a linear correction applied to the absorption bands of the film spectra. The correction is probably not linear if it arises from solubility effects in the alkali halide. However, the corrections are quite small and are not expected to affect the tabulated data appreciably.

3. Preparation of Borates

Borates were prepared using orthoboric acid and the metal carbonate or the metal oxide if the carbonate was unavailable. To reduce the loss of boric acid on ignition most reactions were initiated in aqueous suspensions. The residue on evaporation was subjected to several cycles of heating and grinding until reaction was judged to be complete. For most materials the maximum temperature employed was below the solidus temperature reported in the corresponding phase diagram. However, in the preparation of the alkali borates which crystallized as hydrates from solution, those specimens which melted congruently were melted prior to use. The resulting glasses were crystallized at temperatures below the melting points. The alkali borates that melted incongruently were dehydrated for 24 hr at temperatures 10–20 deg C below the reported incongruent melting points.

For isotope enrichment studies, specimens were prepared using $\text{H}_3\text{B}^{11}\text{O}_3$ (98.3% B^{11}) and $\text{H}_3\text{B}^{10}\text{O}_3$ (96.5% B^{10}) which were obtained from the Oak Ridge National Laboratory. Such pairs of specimens were synthesized in a limited number of cases, usually one for each major structure type expected except in the alkaline earth borates where more were prepared.

Powder x-ray diffraction patterns were obtained on all preparations. The diffraction patterns were checked against reported results where these were available. In many instances powder diffraction data were not available but the x-ray data served to check for contamination by metal oxide or related borates. In many instances the purity of the preparation was checked by means of a polarizing microscope.

In describing the composition of the borates prepared, the following system will be used here and to some extent throughout the paper: The molar ratios will be given with the metal oxide first and the borate as B_2O_3 last. Thus a 4:1 compound will contain 4 moles of metal oxide and 1 mole of boric oxide. Using this convention the following borates were prepared:

1. Lithium borates 1:1, 1:2, 1:3, 1:4, and 1:5 were prepared using the data of Mazzetti and Carli [38] as modified by Sastry and Hummel [46]. The

recent data of Rollet and Bouaziz [45] which show additional 3:1 and 3:2 compounds could not be verified.

2. Sodium borates 2:1, 1:1, 1:2, 1:3, and 1:4 were synthesized in accordance with the phase diagram given by Morey and Merwin [40]. It should be noted that these authors report a 2:1 compound although it is not shown on the phase diagram.

3. Potassium borates 1:1, 1:2, 1:3, 1:4, and 1:5 were prepared using the data of Rollet [44].

4. Calcium borates 3:1, 2:1, 1:1, and 1:2 were prepared in accordance with the diagram given by Carlson [9].

5. Strontium borates 3:1, 2:1, 1:1, and 1:2 were prepared. A phase diagram for the system does not appear to be available to date although Hart and Smallwood [18] apparently have phase equilibrium data. The 1:4 compound corresponding to a known barium borate does not appear to exist.

6. Barium borates 3:1, 1:1, 1:2, and 1:4 were prepared in accordance with the results of Levin and McMurdie [34].

7. Magnesium borates 3:1, 2:1, and 1:1 were prepared using the diagram reported by Davis and Knight [10].

It should be noted that there is some confusion concerning the 1:1 compound which, according to Davis and Knight, decomposes at temperatures above 988°C into B_2O_3 and the 2:1 compound. The powder diffraction pattern in the ASTM file is incorrectly labeled, a point which has been discussed in detail by Block, Burley, Perloff, and Mason [6]. A 1:1 mixture heated at 900°C forms a product which yields a very complex powder diffraction pattern. It cannot be safely concluded that this pattern is free from the 2:1 borate. However, microscopic examination showed that the 1:1 compound prepared in this manner was a single phase differing from the 2:1 compound.

8. Cadmium borates 3:1, 2:1, and 1:2 were prepared. The phase diagram given by Subbarao and Hummel [53] reported 3:2 and 2:3 compounds but no 1:2 compound. The existence of the 3:2 compound was questioned by Hart and Smallwood [18] on the basis of x-ray and infrared data and later by Hand and Krogh-Moe [16]. Results here confirm the absence of the 3:2 compound. Hand and Krogh-Moe [16] have shown that the 2:3 compound is in fact a 1:2 compound.

9. Zinc borates 5:2, 4:3, and 1:2 were prepared. The original work of Ingerson, Morey, and Tuttle on the $\text{ZnO}-\text{B}_2\text{O}_3$ system [22] reported the existence of 5:2 and 1:1 compounds. Harrison and Hummel [17] later confirmed these findings and reported polymorphic forms of both compounds. However, Smith, Garcia-Blanco, and Rivoir [50, 51] showed from single crystal diffraction studies that the 1:1 compound of empirical formula $\text{Zn}(\text{BO}_2)_2$ had the structural formula $\text{Zn}_4\text{O}(\text{BO}_2)_6$ and was therefore a 4:3 compound. Recently Bauer [2], who appeared to be unaware of the previous reports of Smith et al. [50, 51], concluded that the compounds existing in the system were 3:1 (rather than 5:2), 1:1, and 1:2.

Data obtained here by x-ray diffraction and infrared absorption confirm the existence of the 1:2 compound reported by Bauer [2] but are in agreement with the 5:2 ratio rather than the 3:1 value.

10. Lead borates 2:1, 5:4, 1:1, and 1:2 were prepared. The data of Geller and Bunting [13] did not show a 1:1 lead borate but on the basis of x-ray data here it appears probable that this compound exists.

11. Rare earth borates having the ratios 3:1, 1:1, and 1:3 were prepared. Levin, Roth, and Martin [31] have reported on the 1:1 compounds and the 3:1, 1:1, and 1:3 compounds in the $\text{La}_2\text{O}_3\text{--B}_2\text{O}_3$ system were described by Levin, Robbins, and Waring [33]. Further work on the system by Levin and McDaniel [35] shows the existence of some compounds having nominal ratios of 3:1 and 1:3 for many of the other rare earths. Although the exact compositions and properties are not established to date, the materials were prepared for study.

12. Bismuth borates 2:1, 3:5, 1:3, and 1:4 were formed in accordance with the phase diagram of Levin and McDaniel [32].

13. Cobalt borates 3:1 and 2:1 were prepared using the findings of Kononov [23].

14. Miscellaneous borates were prepared as follows:
a. beryllium borate, presumably of composition 3:1 [56].

b. indium borate, 1:1 [31].

c. nickel borate 3:1. This product was formed using NiO. Attempts to prepare the 2:1 nickel borate analogous to the cobalt compound met with no success. The failure to form other compounds might be attributed to the high temperature required to induce reactivity in NiO. The use of NiCO_3 might facilitate formation of other borates.

d. rubidium borate 1:5 [27].

e. cesium borates 1:3 and 1:9 [26].

f. two copper borates which appear in the system $\text{CuO--B}_2\text{O}_3$. One compound is apparently a 3:1 compound, forming large green crystals. The crystals are highly birefringent, biaxial, negative with $2V \approx 15^\circ$, $\alpha = 1.78$, $\beta > 2.00$, $\gamma > 2.00$. The other compound is probably a 1:1 compound and is azure blue. The properties of these crystals have not been determined with certainty. They may be uniaxial negative or biaxial negative.

g. TaBO_4 reported by Zaslavskii and Zvinchuk [61] was prepared with some difficulty. The samples prepared here were not suitable for use because of impurities. The material actually used was supplied by Mrose [41] who has studied this compound in detail.

h. The two isostructural compounds BPO_4 and BaSO_4 , were prepared according to the data of Schulze [49]. Attempts to prepare the antimony analog, BSbO_4 were not successful.

14. Several borates previously reported could not be prepared, in particular, ferrous and manganous borates [6]. Oxidation proceeding in the normal preparation techniques was probably responsible for the failure to obtain these borates.

4. Anion Structure and Vibrational Analysis

4.1. Structures

The fact that a number of borates are formed with the same cation is due to the polymeric behavior of the borate ion. Complex anions can arise from polymerization of basic triangular BO_3 or tetrahedral BO_4 units alone or in combination. The anion structures known to exist have been reported as follows:

The isolated planar anion BO_3^{3-} is found in LuBO_3 , InBO_3 , and ScBO_3 which have the calcite structure [31, 52], in LaBO_3 with the aragonite structure [31], and in $3\text{MgO} \cdot \text{B}_2\text{O}_3$ [5]. The borates isostructural with $3\text{MgO} \cdot \text{B}_2\text{O}_3\text{--}3\text{CoO} \cdot \text{B}_2\text{O}_3$, $3\text{NiO} \cdot \text{B}_2\text{O}_3$, and $3\text{CdO} \cdot \text{B}_2\text{O}_3$ —must also have this anion [42].

The tetrahedral anion BO_4^{5-} has been reported in TaBO_4 [6] and in BPO_4 and BaSO_4 [49].

The pyroborate ion $\text{B}_2\text{O}_5^{2-}$ is formed by connecting two triangular BO_3 groups at one corner. This ion occurs in $2\text{MgO} \cdot \text{B}_2\text{O}_3$ [54] and in $2\text{CoO} \cdot \text{B}_2\text{O}_3$, $2\text{MnO} \cdot \text{B}_2\text{O}_3$, $2\text{FeO} \cdot \text{B}_2\text{O}_3$, and $2\text{CdO} \cdot \text{B}_2\text{O}_3$ [6, 16] which are isostructural.

An infinite chain of BO_3 triangles connected at one corner was shown to be present in $\text{CaO} \cdot \text{B}_2\text{O}_3$ by Zachariasen [36, 58, 59] and in $\alpha\text{-Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ [21].

The boroxol ring, a six-membered ring formed by 3BO_3 groups, contains alternate boron and oxygen atoms and 3 oxygen atoms out of the ring, each connected to one of the boron atoms. This unit occurs in $\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$ [60] and $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ [12, 37]. The rings are interconnected by means of the external oxygen atoms.

Two six-membered rings similar to the boroxol ring are coupled by means of a tetrahedral boron atom common to both rings to form the B_5O_8 anion. This ion is found in $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ and $\text{Rb}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ [27]. Individual B_5O_8 units are interconnected by the external oxygen atoms.

A six-membered ring containing 2 triangular and 1 tetrahedral boron is known in $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$. This unit is connected to similar units through the off-ring oxygen atoms [29].

The basic structural unit in $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ is a $\text{B}_4\text{O}_7^{2-}$ group consisting of 2BO_4 tetrahedra and 2BO_3 triangles. The anion is an 8-membered ring in which the opposite tetrahedral BO_4 groups provide an oxygen bridge. Similar units are interconnected to form a 3 dimensional network [28].

The structure of $\text{BaO} \cdot 2\text{B}_2\text{O}_3$ has been reported to consist of a network containing rings similar to those found in $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$. The two sets of rings are connected by means of the off-ring oxygen atoms and form a 3 dimensional network [7].

Lehmann and Teiss [30] have observed two additional forms of $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ one of which denoted as the β form has a structure similar to that of cristobalite, the other denoted as the γ form appears to be similar to the cubic form of HBO_2 .

Finally, the compound $4\text{ZnO} \cdot 3\text{B}_2\text{O}_3$ contains only tetrahedral boron atoms. The tetrahedra are coupled at certain corners to form a complex 3 dimensional array [50, 51].

The compounds TaBO_4 [61] and BPO_4 and BaSO_4 [49] also contain only tetrahedral boron atoms. In the latter two compounds the borate tetrahedra share corners with PO_4 and AsO_4 tetrahedra, respectively, so that each oxygen atom is part of two different tetrahedra. The empirical formulas of these two compounds could be written BO_2PO_2 and BO_2AsO_2 . TaBO_4 is isostructural with zircon [61] and contains discrete BO_4 tetrahedra.

4.2. Vibrational Analysis

Both the planar triangle and the tetrahedral unit have been discussed in detail many times and only the results will be indicated here [19]. For an isolated, planar, trigonal BO_3 group of D_{3h} symmetry there are four fundamental modes of vibration; ν_1 —the symmetrical stretch, ν_2 —the out-of-plane bend, ν_3 —the antisymmetric stretch, and ν_4 —the in-plane bend. Both ν_3 and ν_4 are doubly degenerate and ν_1 is ordinarily inactive in the infrared. In a given crystalline environment ν_1 may become active and the degeneracies may be removed from ν_3 and ν_4 . The nominal positions expected are ν_1 —950 cm^{-1} , ν_2 —750 cm^{-1} , ν_3 —1250 cm^{-1} , and ν_4 —600 cm^{-1} [57] with the exact positions varying somewhat with the crystal field. An isolated tetrahedral anion of symmetry T_d should also exhibit 4 fundamentals, a normally inactive symmetric stretch— ν_1 , an inactive doubly degenerate mode— ν_2 which involves bond bending, a strongly active triply degenerate stretching mode— ν_3 , and another active bending mode— ν_4 which is also triply degenerate. In a given crystal ν_1 and ν_2 may become active and the degeneracies may be removed from ν_3 , ν_4 . The expected locations of the bands can be inferred from data obtained on similar tetrahedral anions [19]. It is anticipated that ν_3 should occur near 1000 cm^{-1} , ν_1 below 950 cm^{-1} , ν_4 near 600 cm^{-1} and ν_2 below 600 cm^{-1} .

From isotope substitution in the trigonal ion it is expected that ν_1 will be unchanged, $\nu_2^{B_{10}}/\nu_2^{B_{11}} \approx 1.04$ and $\nu_3^{B_{10}\nu_4^{B_{10}}}/\nu_3^{B_{11}\nu_4^{B_{11}}} \approx 1.04$. For the tetrahedral anion ν_1 and ν_2 will be unchanged and $\nu_3^{B_{10}\nu_4^{B_{10}}}/\nu_3^{B_{11}\nu_4^{B_{11}}} \approx 1.04$. In the more complex anions it is possible that vibrations derived from those for the simple triangular or tetrahedral units might be detected. These vibrations would be shifted in frequency by the covalent bonding of the simple units into the complex anion structure but the isotopic frequency shift should serve to give some indication of the nature of the vibrations. As will be shown later, this type of identification which has been referred to as group frequency analysis in connection with spectra of organic materials, may have some justification.

In the pyroborate ion all B—O bonds are not equivalent, as shown by Block et al. [6] in $2\text{MgO} \cdot \text{B}_2\text{O}_3$, and there is no symmetry. The ion is therefore in point group C_1 , all vibrations are of species A and all are infrared active. There are 15 normal modes of vibration and some idea of the nature of these modes may be obtained as follows:

Twelve normal modes would be expected from

internal vibrations of the two coupled triangular units. There should be two each derived from the ν_1 and ν_2 type vibrations and 4 each from the ν_3 and ν_4 types. The extra 3 modes will be derived from the motions of one trigonal unit with respect to the other and arise essentially from the loss of the 3 translational modes of one unit. These latter three modes are expected to be of rather low frequency because of the large masses involved and might lie outside the range of the present studies. The two modes derived from ν_1 and ν_2 can be visualized as in phase and out of phase motions in the coupled triangular units. Those derived from the originally degenerate ν_3 and ν_4 vibrations are somewhat difficult to visualize. However, the effect of isotopic substitution is expected to parallel the behavior of the isolated trigonal ion. Thus modes derived from ν_1 and ν_4 will be relatively unaffected, while those derived from ν_2 and ν_3 will be affected markedly. The three low frequency twisting or rocking modes should also be insensitive to isotopic substitution because of the relatively large masses involved.

The boroxol ring has been studied extensively by Goubeau and his coworkers [14, 15] who have proposed frequency assignments. The B_3O_6 ring is of point group symmetry D_{3h} and of the 21 total normal modes only a few are expected to be normally active in the isolated ring. The active modes are 2 of species A_2'' and 5 of species E' . In metaboric acid Goubeau and Hummel have assigned these bands as follows: species A_2'' ; ν_6 —591 cm^{-1} , ν_7 —476 cm^{-1} ; and species E' ; ν_8 —1375 cm^{-1} , ν_9 —1150 cm^{-1} , ν_{10} —735 cm^{-1} , ν_{11} —456 cm^{-1} , ν_{12} —280 cm^{-1} . From these assignments it appears that not more than 6 fundamentals should be observed for this unit in these experiments, with, ν_{12} below the range studied here.

The other known metaborate structure consists of infinite chains of trigonal borate groups connected through two oxygen atoms. There is no symmetry and all vibrations will be infrared active in species A. The unit cell contains two chains, each of empirical formula $(\text{BO}_2)_4$. The spectrum, therefore, should resemble that of the pyroborate group, as the structural units consist of two coupled pyroborate groups. More bands can be expected because of the larger number of normal modes but the frequencies and isotope dependence should resemble similar data on the pyroborates.

The complex ring systems reported in $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$, $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$, $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, and $\text{BaO} \cdot 2\text{B}_2\text{O}_3$ have no symmetry elements. Therefore, all modes are active and a very complex spectrum is to be expected. No detailed interpretation of these spectra are to be expected unless group frequency analysis should prove useful.

The zinc metaborate structure is very complex and complete analysis is not anticipated. From the x-ray structure analysis [50, 51], in a given tetrahedron one oxygen is connected to a zinc atom while the other 3 atoms are shared by 3 different tetrahedra. Although the structural analysis indicates all B—O

bonds to be similar, this appears to be most unlikely and it seems more reasonable to consider the oxygen coupled to the zinc to be unique. Under these circumstances it is useful to consider the symmetry of the tetrahedral unit to approximate C_{3v} rather than T_d . In this approximation the basic unit can be visualized as containing a central atom bonded to two different kinds of atoms, one the oxygen bound to zinc, and the other, the three oxygens connected into the network. The latter three atoms can be visualized as having large effective masses conferred by the coupling into the other tetrahedra. On the basis of these assumptions the spectrum would be expected to bear some resemblance to that of an XYZ_3 type molecule with allowances for network perturbation effects. As will be shown later this viewpoint permits a reasonable interpretation of the observed data.

5. Presentation of Data

The following system is adopted for presenting the data:

Observed absorption bands are tabulated for each material studied with the following abbreviations used to denote the character of the bands; s—strong, m—medium, w—weak, b—broad, sh—shoulder, v—very. It is understood that the bands may vary in character with the method of obtaining the spectrum, concentration, etc., so that the descriptions apply only to the bands observed here. The existence of the bands listed is considered to be well established because all spectra were obtained at least in duplicate by two different methods. Doubtful bands are indicated with a question mark.

Representative spectra are given for some but not all materials studied with frequencies in wave numbers indicated for the various bands. Two or more spectra are given in each figure with the spectra displaced vertically to eliminate overlapping. The transmittance axis, therefore, cannot be subdivided quantitatively but all spectra are referred to the same intensity scale and are directly comparable. Spectra shown are in most instances composite tracings of mull spectra below 1000 cm^{-1} and film spectra above 1000 cm^{-1} . In some instances film spectra are shown throughout the range used.

Borates are classified with respect to type of anion with all borates of a given type discussed together. Such a separation is desirable because spectra of compounds containing similar anions are expected to be comparable. Although the major separation is in terms of the empirical formula of the anion, subdivision in terms of actual structure is made where the structure is known.

6. Results and Discussion

6.1. Orthoborates

Orthoborates, $X_m(\text{BO}_3)_n$, are formed by the 3:1 divalent metal borates and the 1:1 trivalent metal borates. From the point of view of infrared spectroscopy these compounds may be interpreted, in many

instances, in terms of the simple planar trigonal BO_3^{-3} ion.

a. Divalent Metal Orthoborates

The spectra of all of the divalent metal orthoborates with the exception of $3\text{BeO} \cdot \text{B}_2\text{O}_3$ can be interpreted in terms of the six fundamentals of the perturbed BO_3^{-3} ion. Typical spectra are shown in figures 1 and 2 and the observed bands and assignments are tabulated for the normal isotopic distribution in table 1. The assignments for the bands are supported by the isotopic shifts given in table 2 for some of the compounds. In figure 1 a definite split in the ν_3 band is noted for the B^{11} and B^{10} compounds. The split is not observed in the normal strontium borate although structure in the ν_3 band is apparent. All isotopically "pure" compounds showed such a split which produced two highly unsymmetrical ν_3 bands. The unsymmetrical nature of the bands caused some concern that the apparent splitting might be an artifact caused by variation of index of refraction of the specimen with frequency. Several different experiments were performed using different dispersing media without changing the position or shape of the splitting peak. The split of ν_3 is concluded to be real. Several weak bands in the 750 cm^{-1} — 1000 cm^{-1} region are of uncertain origin. Several of these bands observed in the normal strontium borate are eliminated in the B^{10} and B^{11} compounds so that they may arise from coupling of vibrations between trigonal ions containing different boron isotopes. Such effects have been discussed by Decius [11]. In addition it is not clear from the spectrum or the experiments on isotope substitution which band corresponds to ν_1 . From comparisons with the carbonates and nitrates and from other data to be given later it is concluded that the weak band near 1000 cm^{-1} in these spectra corresponds to ν_1 . The bands near 900 cm^{-1} are taken to represent combinations of lower frequency modes with ν_4 or ν_2 or overtones of a lower frequency mode. The alternate hypothesis that two dissimilar BO_3^{-3} groups are present in the unit cell and give rise to two different symmetric stretching modes is untenable in these compounds. The structure of $3\text{MgO} \cdot \text{B}_2\text{O}_3$ and $3\text{CoO} \cdot \text{B}_2\text{O}_3$ by Burger [35] shows that all BO_3^{-3} groups are equivalent. However, the B—O bonds are not identical and there is no trigonal symmetry. All modes should be active and nondegenerate as shown by the spectra of the isostructural magnesium, cobalt, nickel, and cadmium compounds.

In table 1 the data for $3\text{BaO} \cdot \text{B}_2\text{O}_3$ are incomplete. BaCO_3 contamination produced such strong interferences that the borate bands could not be located with certainty. The known carbonate bands [57] are not listed in table 1. The table lists only limits of the broad, strong ν_3 band. From figure 1 it is clear that the breadth of this band arises in part from overlapping of bands arising from the two boron isotopes. An additional source of strength is probably due to resonance with overtones of ν_4 which fall in this region.

The compounds $3\text{MgO} \cdot \text{B}_2\text{O}_3$, $3\text{NiO} \cdot \text{B}_2\text{O}_3$, $3\text{CoO} \cdot \text{B}_2\text{O}_3$, and $3\text{CdO} \cdot \text{B}_2\text{O}_3$ are isostructural with ortho-

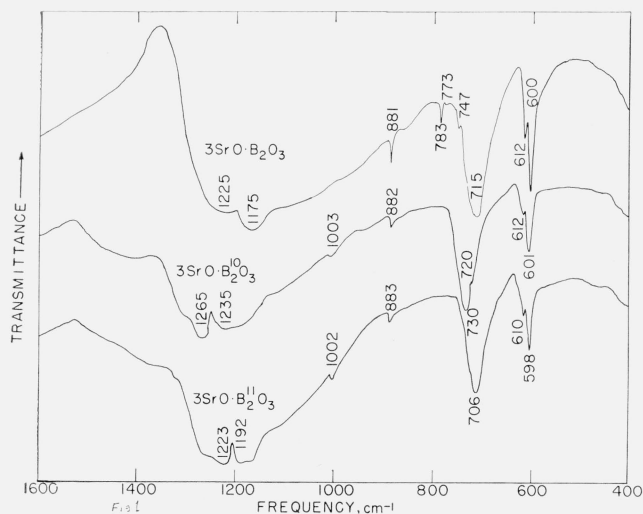


FIGURE 1. Absorption spectra of strontium orthoborates.

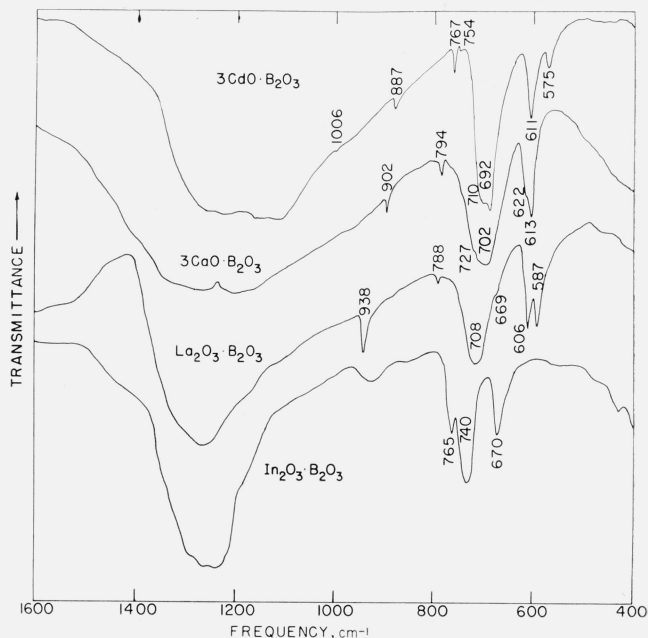


FIGURE 2. Absorption spectra for different crystal structures in the orthoborates.

TABLE 1. Infrared absorption spectra of divalent metal orthoborates (cm⁻¹)

Radius of cation, Å	3MgOB₂O₃ 0.67	3NiOB₂O₃ 0.69	3CoOB₂O₃ 0.73	3CdOB₂O₃ 0.97	3CaOB₂O₃ 0.99	3SrOB₂O₃ 1.12	3BaOB₂O₃¹ 1.34	3BeOB₂O₃
ν_3	1090-1290	1080-1260	1020-1250	1100-1290	1140-1310	1090-1260	1140-1260	1240-1340
ν_1	1022w	893w	893w	1006vw	902w	881w	908w	928m
—	907w	—	—	887w	—	—	—	861s
—	836vw	—	—	—	794w	783w	808w	837w
—	808w	—	—	—	—	—	—	818wsh
		773w	773w	767w	752w	773vw	—	806m
		—	—	754vw	—	747w	—	781m
		709	719	710	727sh	—	—	767s
ν_2	719sb	691vs	676vs	692vs	702vs	715vs	—	740m
		—	—	—	—	—	—	727m
		—	—	—	—	—	—	708m
		—	—	—	—	—	—	700s
		—	—	—	—	—	—	672s
		—	—	—	—	—	—	667msh
		—	—	—	—	—	—	657m
ν_4	657m²	619s²	617s²	611m²	622m	612m	—	649m
		—	—	—	—	—	—	643m
ν_4'	606w	598m	587m	575w	613m²	600s²	—	619w
		—	—	—	—	—	—	600wb
		—	—	—	—	—	—	548wb
		—	—	—	—	—	—	420w
	500sb	400sb	400sb	350sb	420sb	350sb	—	400w

¹ All specimens of 3BaOB₂O₃ were contaminated with BaCO₃. The known absorption bands for BaCO₃ are not tabulated here.

² The stronger of the two bands is denoted by the superscript.

TABLE 2. Infrared absorption spectra of isotopically enriched divalent metal orthoborates

Assignment	3MgOB₂O₃		3CaOB₂O₃		3SrOB₂O₃		3BaOB₂O₃		3CdOB₂O₃	
	B¹⁰	B¹¹	B¹⁰	B¹¹	B¹⁰	B¹¹	B¹⁰	B¹¹	B¹⁰	B¹¹
ν_3	1332	1264	1303	1261	1265	1223	1262	1222	1250	1210
ν_3'	1290	1224	1266	1227	1235	1192	1223	1185	1190	1160
ν_1	1025	1021	1014	1013	1003	1002	—	—	—	—
					882?	883?	—	—	—	—
ν_2	733	720	730	708	729	706	778	749	726	702
							792	761	—	—
ν_4	659	655	624	619	612	610	602	599	608	606
ν_4'	608	604	617	612	601	598	568	567	574	572

rhombic cells having the parameters shown in table 3 [42]. From tables 3 and 1 it will be noted that as the unit cell dimensions decrease, the absorption frequencies generally shift to higher frequencies. This behavior parallels that found previously in isostructural carbonates and nitrates where it was attributed to the effect of anion repulsion in the closer packed structures [57]. For these compounds the behavior of the two components of ν_4 is of interest. It will be noted from table 1 that the higher frequency component of ν_4 is stronger in contrast to $3\text{SrO} \cdot \text{B}_2\text{O}_3$ and $3\text{CaO} \cdot \text{B}_2\text{O}_3$ (figs 1 and 2) in which the lower frequency component of ν_4 is stronger. The amount of splitting between the components of ν_4 appears to be least in the nickel compound and increases as the unit cell gets larger.

TABLE 3. Unit cell parameters of isostructural orthorhombic orthoborates

	a	b	c
	10^{-8}cm	10^{-8}cm	10^{-8}cm
$3\text{MgOB}_2\text{O}_3$	5.398	8.416	4.497
$3\text{NiOB}_2\text{O}_3$	5.398	8.305	4.462
$3\text{CoOB}_2\text{O}_3$	5.642	8.436	4.526
$3\text{CdOB}_2\text{O}_3$	5.967	9.010	4.785

In view of the reversal of intensities in the strontium, calcium, and barium orthoborates it is to be expected that the two groups of compounds are not isostructural. X-ray diffraction shows this to be true and indicates that $3\text{SrO} \cdot \text{B}_2\text{O}_3$, $3\text{CaO} \cdot \text{B}_2\text{O}_3$, and $3\text{BaO} \cdot \text{B}_2\text{O}_3$ might also form an isostructural group. However, even though the details of the structure are unknown, it can be concluded from the infrared spectra that all these compounds contain isolated planar BO_3^{-3} ions. In order for the splitting of ν_3 and ν_4 to occur, the ions must either be nontrigonal or be located in a crystal field of low symmetry.

The assignments given here differ considerably from those of Hart and Smallwood [18] who considered the weak sharp bands near 900 cm^{-1} to correspond to ν_2 and the strong band near 700 cm^{-1} to be ν_4 . In view of the effects of isotopic substitution observed here, these assignments cannot be correct. The error appears to be due to the fact that ν_4 is located outside the spectral range available to Hart and Smallwood [18]. In view of these discrepancies the force constants were recalculated assuming valence forces [19] and the results are tabulated in table 4. The constants shown were calculated using the data of table 2 for compounds containing the B^{11} isotope. The splitting of ν_3 and ν_4 requires at least 2 values for the planar bending constant, K_δ/l^2 , and in this calculation the higher frequency values of ν_3 and ν_4 were considered to represent a corresponding set and the lower frequency values the second set. The value of ν_1 for $3\text{CdO} \cdot \text{B}_2\text{O}_3$ was taken from table 1 and the value for $3\text{BaO} \cdot \text{B}_2\text{O}_3$ which was not observed was assumed to be equal to the value observed in $3\text{SrO} \cdot \text{B}_2\text{O}_3$. As this assumption may be incorrect, data depending on the value are enclosed in parentheses in table 4. The values for the force constants

differ from these given by Hart and Smallwood [18] and are in reasonable good agreement with previous calculations based on the calcite and aragonite forms of the rare earth borates [57].

TABLE 4. Force constants of orthoborate ions assuming valence forces

	K_1	$K\Delta/l^2$	$K\delta/l^2$
	10^5 dyne/cm	10^5 dyne/cm	10^5 dyne/cm
$3\text{MgOB}_2\text{O}_3$	9.82	0.92	0.39
$3\text{CaOB}_2\text{O}_3$	9.67	0.89	0.31
$3\text{SrOB}_2\text{O}_3$	9.42	0.91	0.35
$3\text{BaOB}_2\text{O}_3$	(9.4)	1.0	0.32
$3\text{CdOB}_2\text{O}_3$	9.54	0.87	0.33
			0.30
			(0.31)
			(0.26)
			0.31
			0.26

The spectrum of $3\text{BeO} \cdot \text{B}_2\text{O}_3$ appears to be different from the spectra of the other divalent orthoborates, showing a large number of bands in the 600 cm^{-1} to 850 cm^{-1} range. The differences, however, may be more apparent than real because the spectrum is probably complicated by bands arising from Be-O vibrational modes. BeO itself exhibits broad absorption bands near 960 cm^{-1} , 880 cm^{-1} , and 750 cm^{-1} and the bands in beryllium borate appear to be superimposed on these bands which may arise from excess BeO or from Be-O vibrational modes in the borate itself.

b. Trivalent Metal Orthoborates

This series of orthoborates is of particular interest because of the formation of calcite-, aragonite-, and vaterite-type structures in the borates [31]. Earlier infrared studies demonstrated the similarity of the absorption spectra of the calcite and aragonite type structures [57] but showed no correlation in the spectra of the carbonate and borate vaterites. Later Levin, Roth, and Martin [31] found that the borate-type vaterites all exhibit a transition at elevated temperatures forming a nonquenchable high-temperature phase whose x-ray powder diffraction pattern is more nearly like that of the carbonate vaterite than the diffraction pattern of the room temperature phase. Although it is not possible, at present, to obtain the absorption spectrum of the high temperature phase, it seems probable that it will resemble the spectrum of the carbonate vaterite which can be interpreted on the basis of trigonal CO_3^{-2} ions. The previous data on the borate vaterites could not be interpreted readily in this manner and the problem was unresolved. Isotopic substitution data and comparison with the spectra of other borates permits some conclusions to be drawn at this time.

Considering first the results for calcite and aragonite-type structures, absorption data are compiled in table 5 for $\text{Sc}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ and $\text{In}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ which form calcite-type structures and for $\text{La}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ which forms the aragonite type structure. The spectra of

scandium and indium borates show the spectra associated with the calcite-type structure with ν_1 inactive and ν_4 degenerate and unsplit. Isotopic shifts found with the indium borate confirm the assignments. In the spectra shown in figure 2 the 765 cm^{-1} band observed in $\text{In}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ with a normal isotope distribution can be identified with the ν_2 band of the B^{10} compound by means of the data of table 5. The three bands below 600 cm^{-1} listed in table 5 did not appear in all preparations and were found to be present in In_2O_3 . They presumably arise from excess In_2O_3 .

TABLE 5. Infrared absorption spectra of calcite and aragonite type borates
(cm^{-1})

	$\text{Sc}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ (calcite)	$\text{In}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ (calcite)		$\text{La}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ (aragonite)	
		B^{10}	B^{11}	B^{10}	B^{11}
ν_3	1198svb	1230svb	1202svb	1350sbsh	1310sbsh
ν_1				1289svb	1244svb
ν_2	722sb	765sb	740sb	938m	938m
ν_4	636m	672s	670s	733sb	708sb
				717msh	669wsh
				610m	606m
				591m	587m
		596m	596m		
		560m	561m		
		533m	533m		

The assignments and isotopic shifts in $\text{La}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ confirm the behavior expected for the aragonite type structure. The symmetric stretch, ν_1 , is active and unaffected by the boron isotope, ν_4 , is split and affected slightly by the boron mass, and ν_3 is apparently split and strongly dependent on boron mass. Strong bands at 1350 cm^{-1} and 1310 cm^{-1} were taken to represent the high frequency components of ν_3 for the B^{10} and B^{11} compounds. Alternate assignments as combinations of ν_2 and ν_4 will not satisfy the isotopic dependence observed. In $\text{La}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ with the normal isotopic distribution a band is observed near 790 cm^{-1} (see fig. 2). This band is not found in the isotopically pure compounds and probably arises from coupling effects as noted by Decius [11]. This band was previously found in both neodymium and lanthanum borate and considered to be part of ν_2 . The absence of the band in the isotopically "pure" compounds shows this is not correct. The results obtained here agree well with previous data reported by Steele and Decius [52].

In figure 2 the infrared spectra of the four different crystal structures are compared. The close similarities in the spectra are evident. It will be noted that the behavior of ν_4 in the different structures serves as a distinguishing feature. This band is split in $3\text{CdO} \cdot \text{B}_2\text{O}_3$ with the higher frequency the stronger, it is split in $3\text{CaO} \cdot \text{B}_2\text{O}_3$ with the separation small and the lower frequency the stronger, it is split in $\text{La}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ with both components of about equal intensity but separated about 30 cm^{-1} , and it is unsplit in $\text{In}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$. In the first three compounds the position of ν_4 is about the same but in the $\text{In}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ it has shifted to much higher frequency, an indication of much tighter packing.

Absorption spectra of the rare earth borates having the vaterite type structure were studied only for the holmium, erbium, thulium, ytterbium, and lutecium compounds. Spectra for the holmium, thulium, and ytterbium borates were obtained with the normal isotopic distribution, for lutecium borate in the isotopically enriched compounds only, and for erbium borate in both the normal and enriched forms. Typical spectra are shown in figure 3 for the normal isotopic distribution and in figure 4 for the isotopically "pure" borates of erbium and lutecium. The observed bands are tabulated in table 6.

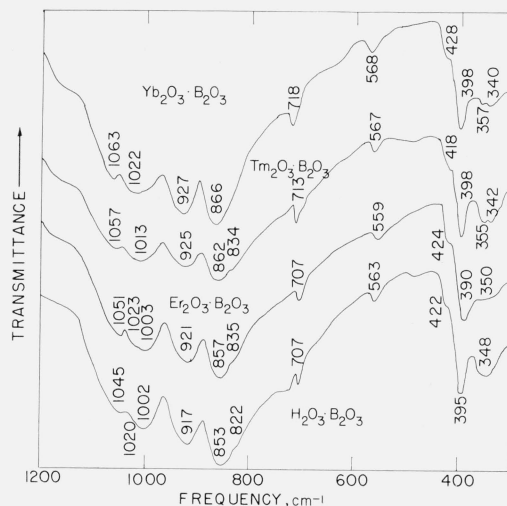


FIGURE 3. Absorption spectra of rare earth vaterite-type borates.

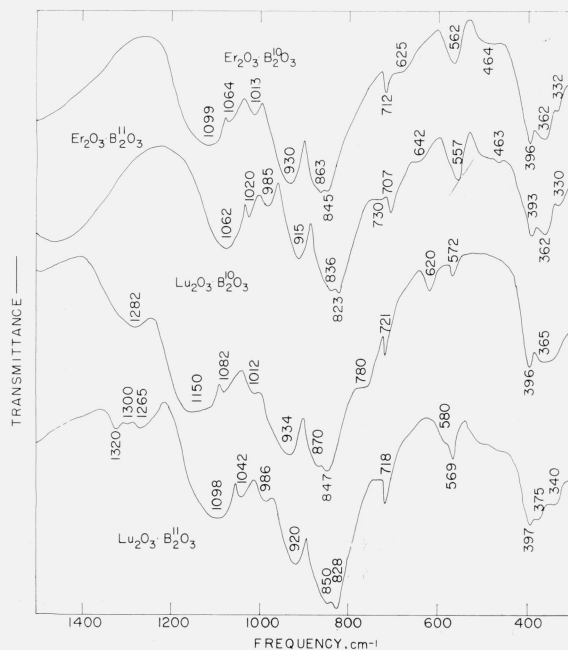


FIGURE 4. Isotope effects in rare earth vaterite-type borates

TABLE 6. Infrared absorption spectra of vaterite type rare earth borates

(cm⁻¹)

Ho ₂ O ₃ B ₂ O ₃	Er ₂ O ₃ B ₂ O ₃			Tm ₂ O ₃ B ₂ O ₃	Yb ₂ O ₃ B ₂ O ₃	Lu ₂ O ₃ B ₂ O ₃	
	B ¹⁰ +B ¹¹	B ¹⁰	B ¹¹			B ¹⁰	B ¹¹
1045sbsh 1020sbsh 1002svb 917sb 853vsb 822bsh	1051bsh 1023sbsh 1003svb 921vsb 857vsb	1099sb 1064m 1013m 930sb 863sb 845s	1062sb 1020m 985m 915sb 836sb 823s 730vw?	1057bsh	1063bsh	1282mvb 1150?mb 1082mb	1320-1265wb 1098svb 1042mb
707m	707m	712m 625bsh 562mb 464bsh	707m 642bsh 557mb 463wsh	713m	718m	1012mb 934sb 870vsb 847vsb 780msh 721m 620mb 572mb	986mb 920sb 850vsb 828vsb
563mb	559mb			567mb	568mb		
424wsh 395s	424wsh 390s	396s	393s	418wsh 398s	428wsh 398s	396s	397s 375sb
348sb	350sb	362sb 332msh	362sb 330msh	355w 342w	357w 340wb	365sb	340mb

In figure 3 it will be noted that the four strong bands between 800cm⁻¹ and 1100 cm⁻¹ confirm the previous observations where only three of these bands could be detected with assurance in all the borates [57]. When isotope substitution is employed it is clear that at least six bands can be resolved in this region. In figure 4 it will be noted that almost without exception each band shifts to higher frequency as the cation mass increases from 167 in Er to 175 in Lu. The same tendency is apparent in figure 3 where the bands are not as well resolved. This shift has been attributed to increased anion repulsion produced by contraction of the unit cell dimensions. The bands between 800 cm⁻¹ and 1100 cm⁻¹ show marked shifts with change in mass of the boron. It is most likely that these bands are fundamentals for the following reasons: first, they are all quite strong, second, the dependence on mass is much greater than to be expected for overtones of low frequency modes, and third, there do not appear to be any reasonably constant differences between these bands. It may be concluded therefore that most of the six strong bands are fundamentals and correspond to a stretching type vibration. The weak bands in the 1300 cm⁻¹ region may be combination modes or arise from contamination with the 3:1 borates whose spectra will be described later.

To interpret these spectra it is necessary to apply certain results which will be demonstrated later. First, every borate which is known to contain trigonal borate groups alone or in complex polymeric anions invariably exhibits strong absorption in the region of 1200 cm⁻¹ or higher. The isotopic mass dependence of these bands shows that they may be considered to be derived from or due to the anti-symmetric stretch of planar BO₃ groups. Second, there is always at least one band attributable to the out-of-plane bending mode of the trigonal group occurring in the 650 cm⁻¹ to 750 cm⁻¹ region which can be identified by its strong isotopic shift. The bands in the 700 cm⁻¹ region for Lu₂O₃·B₂O₃ and Er₂O₃·B₂O₃ do not exhibit an isotopic shift sufficiently large for the trigonal ν₂ band. Third the spectrum of zinc borate which is known to contain

only tetrahedrally coordinated boron shows strong broad fundamentals in the 900 cm⁻¹ to 1100 cm⁻¹ region and a band near 717 cm⁻¹ with a small isotopic shift. From these considerations it is necessary to conclude that the spectra of the rare earth borates of the vaterite type are consistent with the presence of only four-fold coordinated boron in the structure. The longer B—O bonds in the tetrahedra would account for the shift of the strong stretching bands to frequencies below 1100 cm⁻¹. Furthermore, the number of fundamentals observed and their isotopic dependence cannot be reconciled with the behavior to be expected from isolated tetrahedra. These facts lead to the conclusion that the anion in these borates is a complex polymeric structure containing only BO₄ tetrahedra. It is suggested that a six-membered ring containing alternate B—O bonds with each boron connected to 2 off-ring oxygen atoms is not inconsistent with the empirical formula or the spectrum.

6.2. Metaborates

a. Alkali Metaborates

Of the alkali metaborates only the lithium, sodium, and potassium compounds were studied. The spectra of Na₂O·B₂O₃ and K₂O·B₂O₃ are very poor and are characterized by few resolvable bands. Typical spectra are shown in figure 5 and the data are given

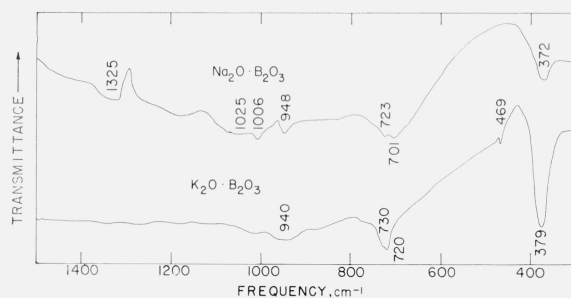


FIGURE 5. Absorption spectra of alkali metaborates.

in table 7. As shown in figure 5 few bands can be resolved in the 1000 cm^{-1} to 1400 cm^{-1} either because of overlapping bands or because of strong scattering. The distortion region below 800 cm^{-1} , however, shows several characteristic bands. From comparisons with previously reported spectra on NaBO_2 [8, 14, 25] it is clear that the present spectrum agrees reasonably well in the distortion region. The strong bands above 1200 cm^{-1} are not distinguishable in the present spectra, however. Using the terminology and assignments of Goubeau and Hummel [14] the 723 cm^{-1} and 701 cm^{-1} bands correspond to two components of ν_{10} in NaBO_2 and the corresponding bands in KBO_2 would be at 730 cm^{-1} and 721 cm^{-1} . The 469 cm^{-1} band observed in KBO_2 but not in NaBO_2 probably corresponds to ν_{11} while the 952 cm^{-1} band in NaBO_2 and the corresponding 940 cm^{-1} band in KBO_2 represent the 1st overtone of ν_{11} . The small discrepancy noted between calculated and observed values for the overtone is not considered significant in view of the breadth of the bands. The bands at 372 cm^{-1} in NaBO_2 and 379 cm^{-1} in KBO_2 are obviously similar but their assignments are not apparent from the data of Goubeau and Hummel [14] except possibly as combinations or overtones of lower frequency modes. Positions of higher frequency bands listed for NaBO_2 are so inexact that they have little significance.

TABLE 7. Infrared absorption spectra of alkali metaborates (cm^{-1})

NaBO_2	KBO_2			LiBO_2		
	$\text{B}^{10} \& \text{B}^{11}$	B^{10}	B^{11}	$\text{B}^{10} \& \text{B}^{11}$	B^{10}	B^{11}
1323svb?				1400svb	1482sb	1435s
					1385sb	1345sb
					1358sb	1316sb
					1298wsh	1160sb
1025svb?					1166sb	1123sb
1006?					1073wb	1072wb
948w	940vb?	942m	942m	973m	986sb	967sb
	775sb			882mb	915sb	895s
741wsh	730ssh	730sb	712sb	810vw	865wsh	877s
				775wsh	778wb	777wb
723s	720s			722sb	722mb	715sb
				685mbsh	715mb	677wsh
701ssh				626mb		620mb
				522sb	545mb	538mb
372m	469w	473w	470w	420mb	510mb	510mb
	379m	382s	381s	406msh	420mb	420mb
					410mb	410mb

As can be seen from table 7 the spectrum of LiBO_2 is completely different from those of the other alkali borates. In the 1000 cm^{-1} to 1400 cm^{-1} region there is overlapping and loss of resolution in the compound with the normal isotopic distribution but in the isotopically enriched specimens the resolution improves and the region is found to contain many bands. From the x-ray powder diffraction pattern, it appears that the LiBO_2 studied here is the α -form and contains anions consisting of chains of BO_3 groups sharing corners [21]. The spectrum should resemble that for $\text{Ca}(\text{BO}_3)_2$ to be discussed later. There are, in fact, many similarities in the spectra of these two compounds, but there are many more absorption bands present in LiBO_2 particularly at the lower fre-

quencies. Because of the small mass of the lithium ion it is expected that vibrational modes arising from motion of the cation might be observed in this spectral region. Such vibrations and their combinations and overtones would be expected to produce a more complex absorption spectrum in LiBO_2 than in $\text{Ca}(\text{BO}_3)_2$. It is also of interest to note that strong bands extend to as high as 1400 cm^{-1} in LiBO_2 . These bands appear to be fundamentals because of their strengths and the fact that their isotopic dependence is inconsistent with overtones and combinations of lower frequency bands. The presence of fundamentals in this range supports the supposition that some of the B—O bonds are much stronger than those found in the BO_3 trigonal ion.

b. Alkaline Earth Metaborates

Typical spectra for the alkaline earth metaborates are shown in figures 6 and 7 and the data for normal isotope distributions are given in table 8 and for isotopically enriched compounds in table 9. The structure of the anion of $\text{CaO} \cdot \text{B}_2\text{O}_3$ is known to consist of endless chains of triangles [36, 58, 59] which may be considered as coupled pyroborate groups. Consequently, the spectrum should resemble that of a pyroborate and the relationship of the bands

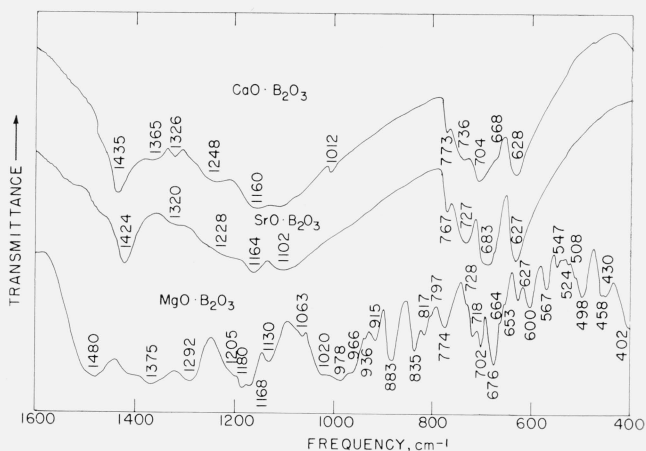


FIGURE 6. Absorption spectra of alkaline earth metaborates.

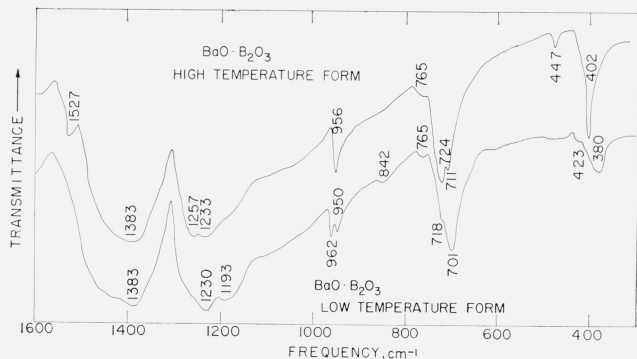


FIGURE 7. Absorption spectra of two forms of barium metaborate.

observed to the fundamentals of a trigonal group should be clear in many instances. Comparing the data of $\text{CaO} \cdot \text{B}_2\text{O}_3$ with that of $2\text{CaO} \cdot \text{B}_2\text{O}_3$ (table 12) it is apparent that the spectra show a close relationship. As in the pyroborate, the group of bands between 1100 cm^{-1} and 1450 cm^{-1} are strong, broad, and very strongly dependent on isotopic mass. These bands are therefore derived from ν_3 of the trigonal group. The 1012 cm^{-1} corresponds to the symmetric stretch derived from ν_1 because it is isotope independent, and the bands below 800 cm^{-1} are derived from the distortion modes ν_2 and ν_4 . The close similarity between the spectra of $\text{CaO} \cdot \text{B}_2\text{O}_3$ and $\text{SrO} \cdot \text{B}_2\text{O}_3$ is apparent in figure 6. This similarity led to the prediction that these compounds were probably isostructural. The prediction was verified by x-ray powder diffraction and it may be concluded that the strontium metaborate also contains anions consisting of chains of BO_3 groups. The spectra of $\text{CaO} \cdot \text{B}_2\text{O}_3$ and $\text{SrO} \cdot \text{B}_2\text{O}_3$ are very simple in view of the large number of active normal modes. Apart from the fact that some bands appear to overlap it seems that many bands must either be very weak or coincide in frequency with other bands to produce a spectrum of such apparent simplicity. Marezio, Plettinger, and Zachariasen [36] recently refined the structure of $\text{CaO} \cdot \text{B}_2\text{O}_3$ and showed that the unique oxygen atom attached to each boron atom in the chain is more tightly bonded than the oxygen atoms of the normal trigonal BO_3 group. This tighter bond can be used to account for the existence of fundamentals of much higher frequency than are normally found in isolated trigonal groups.

TABLE 8. *Infrared absorption spectra of alkaline earth metaborates with normal isotope content*
(cm^{-1})

$\text{Mg}(\text{BO}_2)_2$	$\text{Ca}(\text{BO}_2)_2$	$\text{Sr}(\text{BO}_2)_2$	$\text{Ba}(\text{BO}_2)_2$	
			High temp form	Low temp form
1480b	1435vs	1424s	1527m	
1375vbs	1365m	1320vb	1383sb	1383sb
1292sb	1326m	1228svb	1257s	
1205msh	1248mb		1233sb	1230sb
1180s				
1168s				
1130mb	1160svb	1164s		1193b
1063msh		1102sb		
1020s				
978s	1012vw	1002svb		962m
966s				
936s			956s	950m
915m				842wb
883s				
835s				
817m				
797w				
774m	773m	767m	765wb	765wb
728w				
718m	736mb	727mb	724s	
702s	704sb		711ssh	718ssh
676s				701s
664wsh	668wsh	683sb		
653wsh				
627m	628sb	627sb		
600m				
567m				
547w				
524wsh				
508wsh				
498m	475wb		477w	423wsh
458mb				
430m				
402m			402s	380mb
375m				
355m				

TABLE 9. *Infrared absorption spectra of isotopically enriched alkaline earth metaborates*

$\text{Ca}(\text{BO}_2)_2$		$\text{Ba}(\text{BO}_2)_2$			
B^{10}	B^{11}	Low temp form		High temp form	
		B^{10}	B^{11}	B^{10}	B^{11}
1483sb	1435s	1290	1245	1461	
1411sb	1365m	1271		1422	1367
		1210	1215	1401	
1374sb	1326m	1227	1188	1287	1257
1301sb	1248sb			1275	1230
		966	962		
1163vsb	1168sb?	953	950	957	953m
1012vw	1012w	798		766w	766vw
		786			
781wsh	766m				
		723	700	738s	716s
750m	736m	712	688		
712sb	700s	603vw	604vw		
				480m	476m
675wsh	672sh	388m	388m	400s	400s
		378m	378m		
635sb	627s				

The spectrum of $\text{MgO} \cdot \text{B}_2\text{O}_3$ as shown in figure 6 is quite complex and not analogous to the calcium and strontium compounds. As noted earlier, it is believed that the spectrum is representative of the compound and is not complicated by the presence of other magnesium borates. It appears plausible that because of the tighter packing produced by the small Mg^{+2} ion, the chains present in $\text{CaO} \cdot \text{B}_2\text{O}_3$ and $\text{SrO} \cdot \text{B}_2\text{O}_3$ might be in such close proximity that cross linking by means of the unique atoms might occur. Cross linking would produce some tetrahedral boron atoms and give rise to strong absorption in the 800 cm^{-1} to 1000 cm^{-1} region as shown in figure 6. Some indirect support for this hypothesis may be drawn from the fact that a strongly cross-linked material might be expected to decompose at elevated temperatures, a behavior exhibited by $\text{MgO} \cdot \text{B}_2\text{O}_3$ which decomposes into B_2O_3 and the 2:1 compound. However, some strongly bonded oxygen atoms must be present in the structure as shown by strong absorption bands as high as 1480 cm^{-1} .

Barium metaborate undergoes a transition forming a quenchable high temperature phase and both forms were studied. From the spectra shown in figure 7 it may be concluded that the anion has high symmetry and is unlike the chain anions of $\text{SrO} \cdot \text{B}_2\text{O}_3$ and $\text{CaO} \cdot \text{B}_2\text{O}_3$. Both the low and high temperature forms give similar spectra with some evidence of lowering of the symmetry in the low temperature form as shown by the splitting of the 956 cm^{-1} band into two components at 962 cm^{-1} and 950 cm^{-1} . The isotopic substitution data of table 9 strengthen the indication that bands in the high temperature form split into two components in the low temperature form. Although the structure of the anion is not known in this compound it may be suggested on the basis of the spectrum alone that B_3O_6 rings of the boroxol type may constitute the anion in the high temperature form and that the rings are coupled in some manner in the low temperature form. Single crystal x-ray work, now under way, is expected to confirm or refute the correctness of this suggestion.

in the near future. The x-ray powder diffraction pattern of the high temperature form indexes readily in the hexagonal system with the lattice parameters, $a=7.23 \times 10^{-8}$ cm, $c=39.17 \times 10^{-8}$ cm [7].

c. Zinc Metaborate

Zinc metaborate, the 4:3 compound, has the structural formula $\text{Zn}_4\text{O}(\text{BO}_2)_6$ and represents one of the few anhydrous borates known to contain only tetrahedrally coordinated boron which have been studied in this investigation. Typical spectra for the compound are shown in figure 8 and the corresponding absorption frequencies are tabulated in table 10. The spectra appear to agree well with spectra given by Krogh-Moe [24]. From the structural analysis [50, 51] the B—O bond distance is known to be 1.48 Å and the maximum frequencies observed should be lower than those of any trigonal borate group which has B—O bonds of the order of 1.35 Å. From these considerations it appears likely that the 1082 cm^{-1} band is the highest fundamental and that the weaker bands observed at 1160 cm^{-1} and 1200 cm^{-1} are overtones or combinations. As noted earlier (see 4.2) the spectrum may be assigned completely in this frequency range by considering the bonded tetrahedra to be effective XYZ_3 -type molecules. The assignments given in table 10 were made on this basis using the terminology of Hertzberg [19]. Although the specific assignments are subject to some uncertainty, they show that the three highest frequency bands, i.e., weak broad bands above 1100 cm^{-1} can be interpreted as combinations of the observed fundamentals and an unobserved ν_6 located near 230 cm^{-1} . The internal consistency of the assignments is indicated by the fact that application of the Teller-Redlich product rule [19] to the isotopically enriched specimens gives results in good agreement with the observed frequencies. It is

required that $\nu_1 \nu_2 \nu_3 / \nu_1' \nu_2' \nu_3' = \frac{11}{10} \approx \nu_4 \nu_5 \nu_6 / \nu_4' \nu_5' \nu_6'$

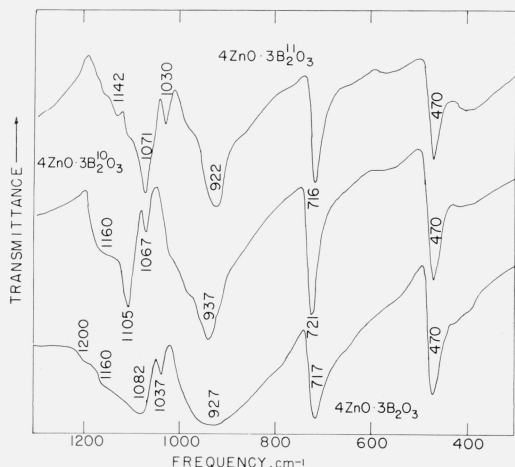


FIGURE 8. Absorption spectra of zinc metaborate ($\text{Zn}_4\text{O}(\text{BO}_2)_6$)

where the unprimed frequencies refer to the B^{10} compound and the primed frequencies to the B^{11} compound. The values of the ratios agree within the experimental error of the measurements with the assumption that the ratio ν_6/ν_6' is unity. It may be noted that both the 470 cm^{-1} and 922 cm^{-1} bands of the B^{11} compound might arise from overtones and/or combinations in view of the derived 230 cm^{-1} frequency. The strength of the bands, however, makes this interpretation unlikely. Some of the internal structure observed in the 922 cm^{-1} band may arise from resonance effects between the fundamental and a combination of ν_4 and ν_6 which would be located near the same frequency.

TABLE 10. Infrared absorption spectra of zinc metaborate $[\text{Zn}_4\text{O}(\text{cm}^{-1})(\text{BO}_2)_6]$

4ZnO·3B ₂ O ₃			Assignment ¹
B ¹⁰ & B ¹¹	B ¹⁰	B ¹¹	
1200wsh	1340vwb	1296vwb	$\nu_5 + \nu_6$
1160wsh	1275wb	1232wb	$\nu_1 + \nu_6$
1082svb	1160wsh	1142wsh	$\nu_2 + \nu_6$
1037m	1105sb	1071sb	$\nu_5(\text{E})$
927vb	1067m	1030m	$\nu_1(\text{A}_1)$
717s	937svb	922svb	$\nu_2(\text{A}_1)$
470s	721s	716s	$\nu_1(\text{E})$
	470s	470s	$\nu_3(\text{A}_1)$
		(230)	$\nu_6(\text{E})$

¹ Assignments on basis of effective C_{3v} symmetry for BO_4 groups.

Regardless of the details of the assignment there is evidence for concluding that no fundamentals occur above 1100 cm^{-1} in the B^{11} compound, a conclusion which is in accord with the weak B—O bond obtained from the x-ray structure analysis. From this result and additional spectra to be discussed later, it is concluded that when tetrahedrally coordinated boron is present strong fundamentals derived from ν_3 of the tetrahedral ion should occur in the 800 cm^{-1} to 1100 cm^{-1} region. In these studies compounds containing three-fold coordinated boron always show strong fundamentals above 1100 cm^{-1} which can be considered as derived from the ν_3 of the trigonal ion. For purposes of determining coordination the region between 800 cm^{-1} and 1400 cm^{-1} is considered to be important. It may also be noted that the zinc metaborate shows a band in the 700 cm^{-1} region. This band might be misinterpreted as corresponding to the out-of-plane mode, ν_2 of a trigonal BO_3 group which falls in the same frequency region. However, isotopic substitution distinguishes these bands because the shift observed in the zinc metaborate is much smaller than the corresponding shift in the trigonal ions.

The rare earth vaterite-type borates (sec. 6.1.b) have spectra showing similarities with the spectrum of zinc metaborate both with respect to band position and with respect to isotope shift. The corresponding bands are 1042 cm^{-1} , 920 cm^{-1} , and 718 cm^{-1} in $\text{Lu}_2\text{O}_3\cdot\text{B}_2^{10}\text{O}_3$ and 1071 cm^{-1} , 922 cm^{-1} and 716 cm^{-1} in $\text{Zn}_4\text{O}(\text{B}^{11}\text{O}_2)_6$. These similarities were considered in

the previous conclusions concerning the presence of tetrahedrally coordinated boron in the vaterite structures.

d. Rare Earth Metaborates

The first few members of the rare earth series form borates having a nominal ratio of metal oxide to boric oxide of 1:3. The composition is known for lanthanum borate [33] but it is less certain for the other borates and the system is presently being studied by Levin and McDaniel [35]. Although the composition is uncertain all the borates will be considered to have the 1:3 ratio at this time. Assuming a 1:3 ratio, the empirical formula can be written $M(\text{BO}_2)_3$ and the compounds can be considered to be metaborates.

Typical absorption spectra are shown in figure 9 and the observed absorption bands are compiled in table 11. From figure 9 it will be observed that there are large numbers of bands throughout the frequency range extending as high as 1450 cm^{-1} . Further it can be observed that there is a very marked correspondence between the spectra, so that it is reasonably certain that the anions are the same or are very closely related in all compounds. The strong broad bands between 1100 cm^{-1} and 1500 cm^{-1} and their large shift with isotopic substitution is indicative of trigonal borate groups. Similarly the strong bands between 800 cm^{-1} and 1100 cm^{-1} and their strong isotopic dependence is indicative of tetrahedral boron. The bands at 725 cm^{-1} and 662 cm^{-1} in $\text{La}_2\text{O}_3\cdot 3\text{B}_2^{11}\text{O}_3$ and their observed shifts may also be taken to indicate the presence of 4-fold and 3-fold coordinated boron, respectively. As shown later, these spectra have many similarities with these of the pentaborates.

TABLE 11. Infrared absorption spectra of rare earth metaborates¹
(cm^{-1})

$\text{La}_2\text{O}_3\cdot 3\text{B}_2\text{O}_3$		$\text{Nd}_2\text{O}_3\cdot 3\text{B}_2\text{O}_3$	$\text{Sm}_2\text{O}_3\cdot 3\text{B}_2\text{O}_3$	$\text{Eu}_2\text{O}_3\cdot 3\text{B}_2\text{O}_3$
B^{10}	B^{11}			
1495sb 1410sb 1380svb	1445sb 1392sb	1456sb 1376sb 1280svb 1210svb	1470svb 1376sb 1308svb 1215sb 1165svb	1460svb 1380sb 1215sb
1183svb 1108sb 1053sb	1167sb 1044sb	1042sb 972s 950m 890svb 808s	1056svb 981s 937wsh 911svb 863msh 813s	1115wsh 1048s 975s 903svb 861msh 810s
964sb 905svb	952sb 870sb	792msh 767m 755msb	795wsh 761s 756s	795wsh 770m 756msh
811sb	789sb	710mb	727s	
776	757m 744msh 725wsh			
730s 717wsh 689sb 661s 614s 578s 523s	662s 605s 572s 516s	672s 612s 580s 522s 492	668s 612s 581m 556m 525s 492	670s 611s 583sb 556s 524sb 490

¹ The molar ratio of only $\text{La}_2\text{O}_3\cdot 3\text{B}_2\text{O}_3$ is known. The others are not known. X-ray diffraction and phase equilibrium data indicate that the europium and possibly samarium may have different compositions from that given here.

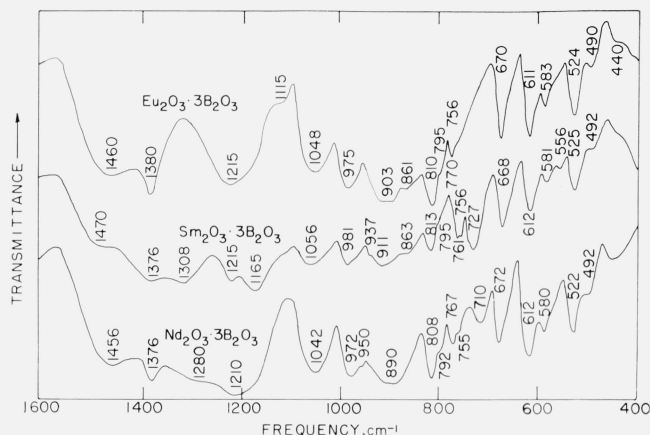


FIGURE 9. Absorption spectra of rare earth metaborates.

6.3. Pyroborates

The divalent metals form compounds with a 2:1 ratio of oxides which have empirical formulas $\text{X}_2\text{B}_2\text{O}_5$ and can be classed as pyroborates. Typical spectra are shown in figure 10 and the absorption bands are tabulated in table 12. From the figure it is observed that the spectra are quite similar and are of intermediate complexity. The lead pyroborate, however, as shown by the tabular data is somewhat different. Considering first the isotopic substitution data on $2\text{CaO}\cdot\text{B}_2^{11}\text{O}_3$, the two modes derived from ν_2 of the trigonal ion are probably represented by the 723 cm^{-1} and 713 cm^{-1} bands tabulated for the B^{11} compound. The 713 cm^{-1} band is not shown in figure 10 but is frequently resolved as a shoulder on the 723 cm^{-1} band. The overlap of the two modes is believed to produce the rather broad intense band above 700 cm^{-1} in all spectra of figure 10. The bands at 670 cm^{-1} and 618 cm^{-1} are identified by their relative independence of isotope mass as two of the modes derived from ν_4 . The other two components of ν_4 are not apparent. They may be too weak to be observed, may coincide in frequency with the observed bands, or may overlap the band at 723 cm^{-1} which is apparently complex. The 474 cm^{-1} mode is probably an ionic distortion mode and may be tentatively assigned as the coupled bending mode. Two twisting modes probably are beyond the frequency range used. The symmetric stretch can be identified with the isotope independent frequency at 1012 cm^{-1} . The other mode derived from ν_1 is not apparent and may correspond to the 803 cm^{-1} band. This band, however, may also originate from combinations or overtones from a low frequency mode. The four modes derived from ν_3 of the trigonal ion are located between 1150 cm^{-1} and 1400 cm^{-1} . There are at least six bands observed in this region for $2\text{CaO}\cdot\text{B}_2^{11}\text{O}_3$ and at least two of these— 1177 cm^{-1} and 1450 cm^{-1} —may be combinations or overtones. Therefore, with reasonable assurance the bands of table 12 can be assigned to the $\text{B}_2\text{O}_5^{4-}$ ion in terms of the corresponding vibrations of the

TABLE 12. *Infrared absorption spectra of divalent pyroborates*
(cm⁻¹)

2MgOB ₂ O ₃	2CaO·B ₂ O ₃			2SrOB ₂ O ₃	2CdOB ₂ O ₃	2CoOB ₂ O ₃	2PbOB ₂ O ₃
	B ¹⁰ &B ¹¹	B ¹⁰	B ¹¹				
1450vs vb		1450msh	1450msh				
	1366	1411vs	1365vs	1350sb	1350s vb	1400s vb	1352w
1290m	1328	1374s	1327s	1323sb			1315sh
1260m	1292	1335s	1290s	1261sb			1284s
	1248	1302vs	1255vs	1220sb	1250sb	1250s vb	1248s
1150s vb	1140s vb	1208ssh	1177ssh				1233s
		1172	1158s vb	1161sb	1130s vb	1150s vb	
1022m	1011m	1012m	1127sbsh	1092sb			1017sb
975bsh	973vw		1012m	1000m	998m	1007	971s
834wb							877vs
	806w	813m	803m	789w	800	817	835
789wb	775vw			772w			
745msh				735msh			744m
				726msh			731m
712s	718s	738s	723s	717s	707		
		735s			691s	698s	710
683s		728sh				693	703
668msh	667m	671s	670s	656m	667s	658	685bsh
							661
603s	618s	618s	618s	616s	591s	587	640
							615
568w							595
535wsh						572	578
484s	475w	475	474w	460w	497w	449	547m

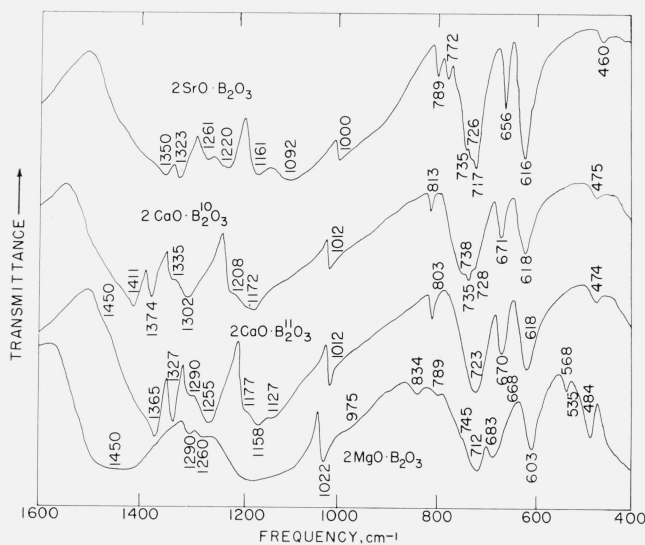


FIGURE 10. *Absorption spectra of pyroborates.*

parent BO_3^{3-} group. It is of interest to note that although the symmetric type stretching frequency in the pyroborates is essentially the same in the orthoborates, modes derived from ν_3 of the trigonal ion extend to much higher frequencies. The higher frequencies are not unexpected in this case because all B—O bonds are not equivalent in the pyroborates [6] and a greater partial double bond character may be attributed to some bonds.

From the data of table 12 it can be observed that the lead pyroborate exhibits a spectrum similar to the other pyroborates but containing more bands, particularly several strong bands in 800 cm^{-1} to

1100 cm^{-1} region. There are also other bands at lower frequencies not found in the other pyroborates. Therefore, the anion in this compound probably does not consist of two coupled trigonal groups. The bands in the 800 cm^{-1} to 1100 cm^{-1} region may be taken to indicate that tetrahedral boron is present and the low frequency bands are indicative of a large complex anion.

6.4. Triborates

Alkali borates formed with the 1:3 ratio of oxides have the empirical formula XB_3O_5 . For purposes of this discussion they are classed as triborates. No structural data appear to be available on the compounds studied except $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ [29]. The anion is quite complex and is composed of six-membered rings each containing 2 triangular and one tetrahedral boron, with the tetrahedral boron atoms being shared by two rings. Typical spectra are given in figure 11 for the isotopically substituted lithium compounds with the observed data being tabulated in table 13. From figure 11 it can be observed that the spectra are complex and indicative of a low symmetry and a large anion. The spectra are consistent with the presence of both trigonal and tetrahedral boron. The persistence of absorption bands which appear to be fundamentals to high frequencies is indicative that at least some of the B—O bonds have partial double bond character. The spectra and the shifts observed are not inconsistent with the six membered ring found in $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ although the spectra are too complex to warrant any specific conclusions on this point without further information on the origin of the various bands.

TABLE 13. Infrared absorption spectra of alkali tetraborates (XB_3O_5)

$\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$			$\text{Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3$	$\text{K}_2\text{O} \cdot 3\text{B}_2\text{O}_3$	$\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$
$\text{B}^{10} \text{ \& \& B}^{11}$	B^{10}	B^{11}			
1490sb 1365sb 1258sb	1540vsb 1410svd 1280vsb	1490vsb 1365svb 1258svb	strong broad bands to 1450	strong broad bands to 1450	1455mb 1330mb 1320sb 1250vsb
1083sb	1097sb	1080sb	1270svb 1228sb 1137mb 1070sb 1040sb	1250-1280 1227sb 1110mb 1073mb 1030msh	1080sb 1012msh 967sb
992sbsh 954vb	1007ssh 986sb 970sb	992ssh 957sb	970bsh 938s	966sb 937sb	
913b		913mb	901sb	892sb	907svb
882sb 849b 771s 755msh	928mb 900mb 864mb 781m 762msh	885mb 847svb 774m 758msh	850sb 818s 777msh 768s 757wsh	862sb	847sb 797sb 777msh 759s 749s
730s 723msh	740m 730msh	723mb		758w 746m 735m 720mb	
682msh 667m		680m 671m	701m 684m 673m	692m 686wsh 663w 654w 646w	702sb
644m	686mb 653mb	662mb 639m	643w 637w		652mb
602w 572s 547w 528m 501w	575mb 528m	600mb? 567mb 525m	564m 549m 530s 507s 500wsh 493msh 469s 456wsh 431w	601w 567wb 522s	563w 547w 530s 510s
455s	455mb	454m		450m	474msh 459s
412w 382m 355m	431m 412m 386m	430 410m 380m			

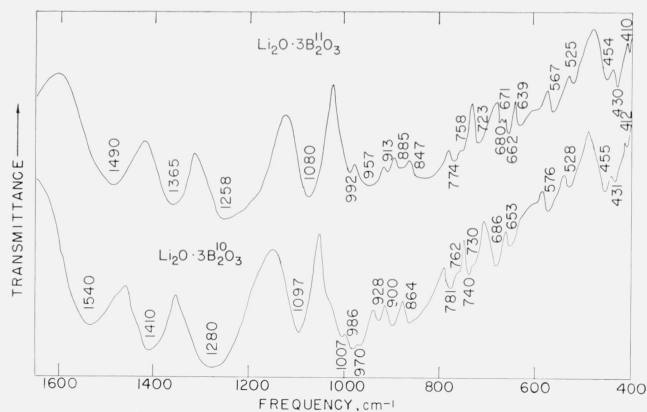


FIGURE 11. Absorption spectra of lithium tetraborates.

6.5. Tetraborates (XnB_4O_7)

Both monovalent (alkali) and divalent metals form borates in a 1:2 ratio of oxides which have empirical formulas $\text{X}_2\text{B}_4\text{O}_7$ and YB_4O_7 , respectively. These compounds are classified as tetraborates.

a. Alkali Tetraborates

From the structure of lithium tetraborate reported by Krogh-Moe [28] it is expected that the spectra of the alkali tetraborates might give evidence for both 3- and 4-fold coordinated boron in a complex ring

system of low symmetry. The spectra shown in figure 12 and the data of table 14 show that the results are in accord with the predictions. The strong bands and the isotopic shifts in $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ in the 800 cm^{-1} to 1100 cm^{-1} region are indicative of tetrahedrally coordinated boron and the similar bands in the 1100 cm^{-1} to 1400 cm^{-1} region are indicative of 3-fold coordination. Similarly the 773 cm^{-1} and 676 cm^{-1} bands of the B^{11} compound are taken as indicative of the presence of the two types of boron. These conclusions have been verified by the NMR data of Ring and Bray [43]. The absorption at higher frequencies is strong and broad and is not tabulated for the compounds with the normal isotopic distribution. These bands, however, are resolved in the two isotopically substituted lithium tetraborates. There is a very close correlation between the spectra of the sodium and potassium tetraborates and the anions in these compounds are apparently identical but it is not clear from the spectra that the anion in $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ is similar. In the case of the sodium and potassium compounds the correlation is so close that it is suspected that they may be isostructural. The data obtained on $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ appear to agree reasonably well with the spectrum given by Krogh-Moe [25]. It may be noted that some of the apparent discrepancies between the data for the lithium tetraborate and the sodium and potassium tetraborates may arise from the tighter packing which presumably occurs with the small lithium ion.

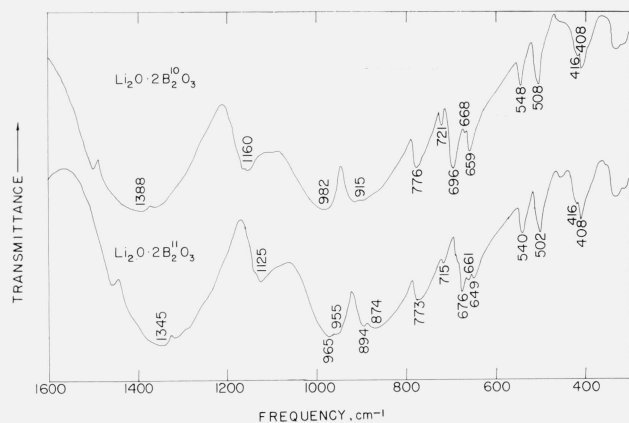


FIGURE 12. Absorption spectra of alkali tetraborates.

TABLE 14. Infrared absorption spectra of alkali tetraborates ($X_2B_4O_7$) (cm^{-1})

Li ₂ O·2B ₂ O ₃			Na ₂ O·2B ₂ O ₃	K ₂ O·2B ₂ O ₃
B ¹⁰ &B ¹¹	B ¹⁰	B ¹¹		
	1388vsb 1160sb	1345svb 1125sb	1148sb 1090sb 1046sb 1010sb	1130msh 1085mb 1032sb 978sb
970sb	982svb	965sb	900—	915—
886sb	-----	955ssh 894ssh	836svb	835svb
861sb	915svb	874svb	779	779
771s	776sb	773sb	767m 745sh 725 717	763 748 730 718
718msh 707msh 678m 650mb	721m	715m	675mb 661m 636m 611m 583m 554m 513m 490w 472w	670msh 660m 637m 612m 596s 553m 517m 492w 476w
596msh 566wsh 543s 508msh 504s 455w	696s 668w 659s 548s 508s 416sh 408s	676s 661msh 649msh 540s 502s 416sh 408s	-----	-----

b. Divalent Metal Tetraborates

The divalent metal tetraborates fall into two distinct groups with respect to their infrared spectra. Typical spectra for one type are shown in figure 13 and the data for all the compounds studied are compiled in table 15. From the tabulated absorption data it is clear that strong absorption occurs at much higher frequencies in the spectra of the calcium, barium, and zinc compounds than in those of strontium and lead. The presence of both 3-fold and 4-fold coordinated boron is indicated in the former compounds with a large anion of low symmetry. The structure reported for $BaO \cdot 2B_2O_3$ fulfills these requirements [7]. Although the tabular data indicate that the spectra of $CaO \cdot 2B_2O_3$ and $ZnO \cdot 2B_2O_3$ are very similar, this does not appear to be true. Comparison of the actual spectra shows marked differences in positions and relative intensities of many bands. On the basis of these

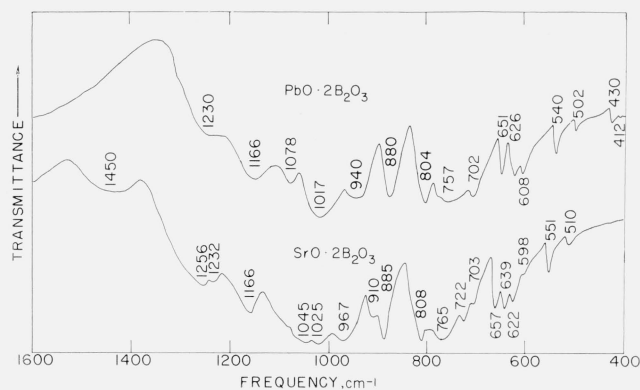


FIGURE 13. Absorption spectra of divalent metal tetraborates.

data it seems improbable that the anions in these compounds are identical.

From figure 13, however, it can be seen that the spectra of $SrO \cdot 2B_2O_3$ and $PbO \cdot 2B_2O_3$ are so similar that a structural relationship is indicated. X-ray powder diffraction patterns show that these two compounds are isostructural [7]. The spectra may be interpreted in the usual manner to indicate tetrahedrally coordinated boron. There appear to be bands in the region above 1100 cm^{-1} which would ordinarily be taken as indicative of the presence of boron in 3-fold coordination. However, bands in this region are not intense, being much weaker than expected for fundamentals presumed to be related to the ν_3 mode of triangular units. Therefore, it seems probable that these bands may represent overtones or combinations of some of the lower frequency modes. Although there is some evidence for the presence of boron in 3-fold coordination in the isotopic shifts observed for some bands in the 700 cm^{-1} region, the evidence cannot be considered unequivocal in the presence of such a complex spectrum. It is clear that the anions in these compounds are probably identical and complex. On the basis of the infrared spectrum it is concluded that the anions consist of tetrahedrally coordinated boron atoms with the presence of *any* boron in 3-fold coordination being doubtful. These conclusions are substantiated by the rather high density reported for $SrO \cdot 2B_2O_3$ [7].

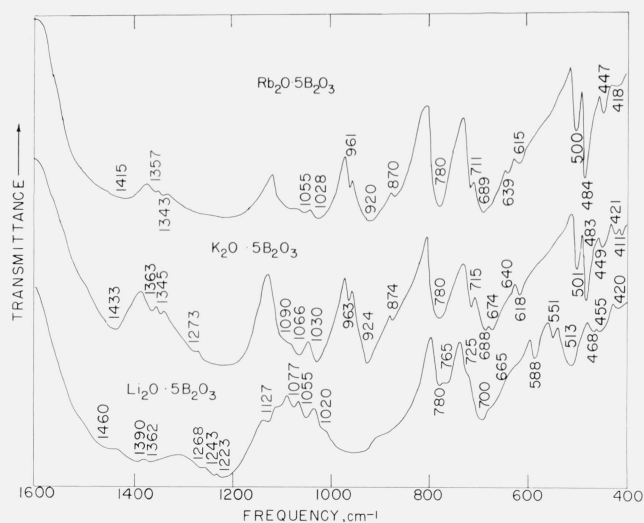
Note added in proof: Work on the crystal structure of $SrO \cdot 2B_2O_3$ and $PbO \cdot 2B_2O_3$ has been completed by S. Block and A. Perloff. The structure, reported at the Annual Meeting of the American Crystallographic Association in Bozeman, Mont., July 1964, is found to contain only tetrahedral boron atoms. This result confirms the conclusions drawn from spectroscopic evidence alone. A paper on the structure is in preparation.

6.6. Pentaborates (XB_5O_8)

Some alkalis form compounds having a 1:5 ratio of the oxides and an empirical formula XB_5O_8 which are classified here as pentaborates. From the known structures [27] it is expected that the spectra should be complex and show evidence for both trigonal and tetrahedral boron. The spectra shown in figure 14 and the tabulated data of table 16 verify this prediction. In figure 14 it can be noted that the

(cm^{-1})

CaO-2B ₂ O ₃	BaO-2B ₂ O ₃	ZnO-2B ₂ O ₃	SrO-2B ₂ O ₃			PbO-2B ₂ O ₃
			B ¹⁰ & B ¹¹	B ¹⁰	B ¹¹	
1435sb	1443mb		1450mvb			
1390sb	1400mb	1390sb				
1363sb	1332-	1342sb				
1305sb	1292svb	1298sb				
1247sb	1245sb	1260sb	1256sb			
1188sb	1163m	1237sb	1232sb	1260sb	1223sb	1230sb
		1192msh				
		1165sb	1166sb	1168sb	1157sb	1166s
1090sb	1082wsh	1072sb	1045sb	1080-	1060-	1078sb
1052sb	1068mb	1047wsh	1025sb	970vsvb	950vsvb	1017sb
993sb	995sb	988sb	967sb			940sb
942sb	926sb	965	910mb			
910sb	887sb	906sb				
850sb	835sb	858sb	885s	891s	905msh	
815mb		832m			880s	880sb
793wsh	790m	810m	808s	811s	806s	804s
776mb	761m	763msh	765sb	769sb	750sb	757sb
728m	735sb					
706s	711m	716s	722m	731s	717ssh	
691wsh	679s	698msh	703m	702ssh	700ssh	702s
668m	660m	672w				
658wsh	653w	655w	657s	669s	653s	651s
632		643wb	639s	646m	636m	626s
600	606s			633vw	629vw	
	592w		622s	619s	618s	608s
585	580w	582w	598msh		601wsh	
567s	557m	561m			581w	
534m	529	545			566wsh	
505	496m		551s	549s	549s	540s
	483	469s			540msh	
	451s		510w	508s	508s	502s
	388m			442	435	430m
				411	411	412w
			358m	357s	356s	342w



close similarity between the spectra of the rubidium and potassium compounds is indicative of their isostructural relationship [27]. The positions and isotopic shifts shown for the potassium pentaborate in table 16 are indicative of both 3-fold and 4-fold coordinated boron atoms. In the isotopically substituted compounds there appear to be several sets of “doublets” consisting of bands of equal strength, with a small separation, and similar isotopic shifts. Apparently overlapping of bands from B^{10} and B^{11} compounds obscure these doublets in the spectrum

TABLE 16. *Infrared absorption spectra of alkali pentaborates*
(XB_5O_8)

 (cm^{-1})

Li ₂ O·5B ₂ O ₃	K ₂ O·5B ₂ O ₃			Rb ₂ O·5B ₂ O ₃
	B ¹⁰ & B ¹¹	B ¹⁰	B ¹¹	
1400–1300	1433sb	1468sb	1419sb	1415svb
1275–1175vsb	1363m	1405m	1359s	1357m
1127m	1345m	1387m	1338m	1343m
1077m	1273sh	1372m	1334m	
	1250–1190b	1257svb	1202svb	1250–1150svb
	1090bsh			
1055m	1066s	1084m	1061m	1055m
1020bsh	1030s	1040svb	1030svb	1028svb
	963m	974ssh	962s	961m
1010–875svb	924sb	940svb	923svb	920sb
	874s	877s	872s	870s
780s				
765s	780s	791s	780s	780sb
725msh	715s	732s	714s	711s
		711s		
700sb	688s	702s	684s	689sb
665ssh	674s	692msh	673ssh	670msh
	640wsh	660msh	635msh	639m
		636m		
588m	618m	630m	616m	615m
551m		508s	503s	509s
513m	501s	504s	500s	500s
468w	483s	489s	483s	484s
455w	449m	452w	449w	447m
	421w	422w	421w	
420w	411w	412w	412w	418w

The anions of the potassium and rubidium compounds may be considered as coupled modified boroxol rings. The presence of the tetrahedral boron should tend to decrease the strength of some of the B-O bonds in the ring and the coupling should tend to increase the effective mass of the coupling boron atom. Both effects would tend to decrease some observed frequencies below the corresponding modes of the boroxol ring. Furthermore from the lack of symmetry all modes of the modified boroxol ring should be active in this instance. Comparison of these spectra with those of the alkali metaborates is not too informative because of the poor spectra of the metaborates and their low infrared activity arising from symmetry. The only mode common to both compounds appears to be represented by the strong band identified as ν_{10} [14] in the alkali metaborates. This band occurs at 723 cm^{-1} in NaBO_2 at 712 cm^{-1} in KBO_2 , 711 cm^{-1} in $\text{Rb}_2\text{O} \cdot 5\text{B}_2\text{O}_3$, and 714 cm^{-1} in $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$. The position, character, and isotopic shift noted in the KBO_2 and $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ compounds are so similar that this band can be assigned tentatively as corresponding to ν_{10} (E'). Comparing the present data with these of Goubeau and Keller; the following tentative assignments may be made in the pentaborates: for $\text{Rb}_2\text{O} \cdot 5\text{B}_2\text{O}_3$, ν_1 (A_1') $1150\text{--}1250\text{ cm}^{-1}$, ν_2 (A_1') 780 cm^{-1} , ν_3 (A_1') 500 cm^{-1} or 509 cm^{-1} , ν_{10} (E') 711 cm^{-1} ; for $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$, ν_1 1190 cm^{-1} 1250 cm^{-1} ; ν_2 (A_1') 780 cm^{-1} , ν_3 (A_1') 501 cm^{-1} or 508 cm^{-1} , ν_{10} (E') 715 cm^{-1} . It is also expected that ν_9 (E') may fall in the regions given for ν_1' contributing to the strength and broadness of these bands. The bands at 484 cm^{-1} and 483 cm^{-1} in the pentaborates probably correspond to ν_7 (A_2') which are strongly active in these compounds because of low symmetry. With this assignment it seems probable that the bands at 963 cm^{-1} and 961 cm^{-1} are the first overtones of ν_7 . Although these assignments can only be taken as possibilities the relative insensitivity of these band positions to the substituents as demonstrated by Goubeau and Keller [15] lends some support to the proposed assignment.

6.7. Octoborates ($\text{X}_n\text{B}_8\text{O}_{13}$)

The alkali metals together with barium of the alkaline earth metals form borates with a 1:4 ratio of the oxides. The empirical formula of the anion is $\text{B}_8\text{O}_{13}^{2-}$, classified here as an octaborate. Typical spectra of these compounds are given in figure 15 and the data obtained are compiled in table 17. As expected and as shown in figure 15 a spectrum extremely rich with bands is obtained. All compounds show bands in positions taken to be characteristic of both 3-fold and 4-fold coordination of boron, and the isotopic shifts observed with lithium octaborate strengthens this conclusion. From the spectral data alone it seems very unlikely that the same anion is present in any of these compounds. Lithium octaborate in particular shows a large number of absorption bands but these may be due

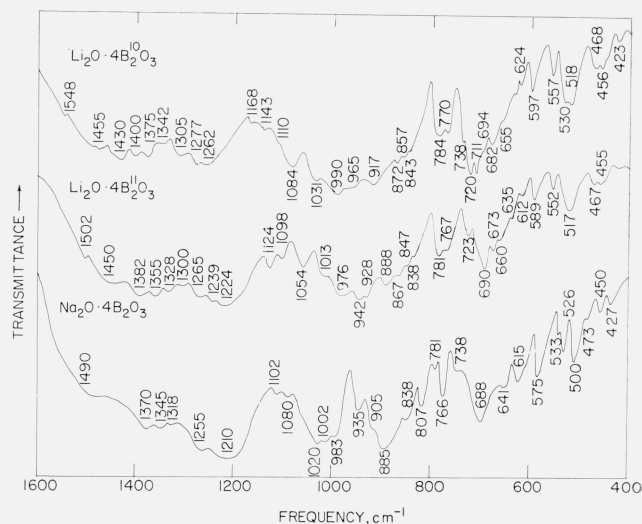


FIGURE 15. Absorption spectra of alkali octoborates.

in part to Li-O vibrational modes, detected in this range because of the small mass of the cation. No structural data are available to assist in the interpretation and without some information of this type any attempt to explain these spectra is of dubious value.

TABLE 17. Infrared absorption spectra of the octoborates ($\text{X}_n\text{B}_8\text{O}_{13}$) (cm^{-1})

$\text{Li}_2\text{O} \cdot 4\text{B}_2\text{O}_3$		$\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	$\text{K}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	$\text{BaO} \cdot 4\text{B}_2\text{O}_3$
B^{10}	B^{11}			
1548sb	1502sb			
1455svb	1450svb			
1430sb	1382sb	1490svb	1425svb	1420-1320svb
1400sb	1355sb	1370sb		
1375sb	1328sb	1345sb	1357svb	
1342sb	1300svb	1318mb	1312svb	
1305sb	1265sb			
1277sb	1239sb	1255sb		1268sb
1262sb	1224sb			
1168sb	1124mb	1210svb	1192svb	1227sb
1143sb	1098m			1190sb
1110msh	1074msh	1102mb		1095sb
1084sb	1054m	1080mb	1066sb	1075mb
1031m	1013msh			
990sb	976sb	1020sb	1034sb	
965sb	942sb	1002mb		
	928msh	983msh	961msh	968svb
		935m	925svb	
		905msh		890mb
		885sb		865mb
917sb	888mb			
872m	867bsh		872msh	
857m	847bsh			
843msh	838ssh			
		838msh		
784sb	781s	807s	787mb	795mb
		781w		
770s	767s	766s	775mb	765mb
738msh	723m	738msh	716mb	723sb
720s		702msh		
711s	690s	688s	686mvb	698mb
694msh	673m			673mb
682m	660w		668m	655mb
655msh	635w			
624m	612m	641m		593sb
597s	589m	615m		
557m	552m	575s		544msh
530s				
518s	518sb	533m	500s	515s
		526s		
		500s		
468m	467m	473w	484s	490sb
456m	455m	450m	449m	
423w		427m		

6.8. Miscellaneous Borates

In this section data are presented for those borates which cannot be readily classified in the previous categories. These will represent in most instances individual borates of odd compositions or groups of borates whose classification as to anion type is obviously of no value.

a. Rare Earth 3:1 Borates

Levin and McDaniel [35] have observed that the rare earths form borates having a nominal oxide ratio of 3:1. There is doubt at this time that the ratio remains constant throughout the series of rare earth borates but there is no question that the compounds are formed. Inasmuch as the rare earth oxides produce no appreciable absorption in the frequency range used here, satisfactory spectra of the desired borates will be obtained if the quantity of oxide is in excess of the amount required for compound formation. If, as now appears likely, the compounds are of the 3:1 ratios or less, materials formed by a 3:1 oxide ratio should produce spectra of the borate only. From powder x-ray diffraction data on the compounds it is found that the 3:1 compounds of lanthanum, praseodymium, and neodymium are most probably isostructural. From samarium to ytterbium, however, a new structure or perhaps new structures (and probably different compositions) appear to form. This behavior is observed in typical spectra shown in figures 16 and 17 and the data tabulated in table 18. It is noted in figure 16 that the spectrum is characteristic of trigonal BO_3 groups with bands derived from the 4 modes of the trigonal ion apparent. The isotopic substitution effects shown for the lanthanum compound in figure 16 show that the bands in the 1200 cm^{-1} region are analogous to ν_3 , the 937 cm^{-1} band to ν_1 , the 700 cm^{-1} region bands to ν_2 and the 600 cm^{-1} region bands to ν_4 of the trigonal ion. However, at least 3 bands appear in each of the ν_3 , ν_2 , and ν_4 regions and the spectra are not typical of isolated trigonal ions. They are also not typical of either the pyroborate ion, the boroxol ring, or chains of triangular groups. It appears that the spectra of the first few members of the 3:1 rare earth borates are indicative of a new type of anion which is most probably a polymer formed of BO_3 groups.

Starting at $3\text{Eu}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ and continuing to $3\text{Tm}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ the marked change observed in figure 17 occurs in these spectra. Strong bands in the 800 cm^{-1} to 1100 cm^{-1} range occur which are indicative of boron with 4-fold coordination. Simultaneously new absorption bands appear in the 700 cm^{-1} to 800 cm^{-1} region which tend to confirm the indication. As the increase in atomic weight in the rare earth series is accompanied by a decrease in ionic radius, it would be expected that the packing in the unit cell increases as the mass of the cation increases. In the anion, however, closer packing can be accomplished by increase in coordination of boron from 3 to 4.

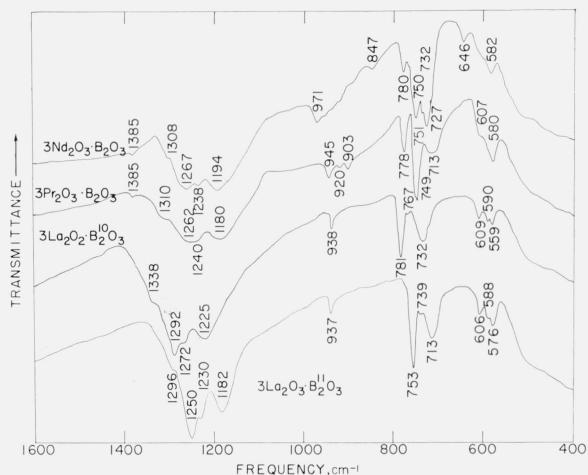


FIGURE 16. Absorption spectra of 3:1 rare earth borates.

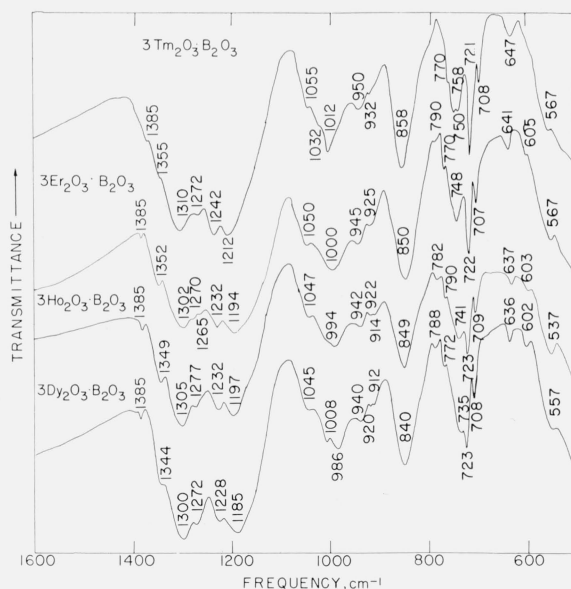


FIGURE 17. Absorption spectra of 3:1 rare earth borates.

Therefore, the increase in coordination indicated by these spectra is not surprising, and it would not be surprising if the composition of the compounds also changed. It should be noted, however, that there is still evidence for boron in 3-fold coordination in addition to the 4-fold coordination so that the anions are probably quite complex.

b. Bismuth Borates

The bismuth borates form in ratios of oxides which are unlike the other trivalent ions in most instances and the spectra of all the compounds are discussed here. No isotopically pure compounds were prepared for these compounds. Typical spectra are shown in figure 18 and the absorption frequencies are tabulated in table 19. The spectra of figure 18 all exhibit strong bands to low frequencies as well as

TABLE 18.—Infrared absorption spectra of the 3:1 rare earth borates

		(cm ⁻¹)			
3La ₂ O ₃ B ₂ O ₃		3Pr ₂ O ₃ B ₂ O ₃	3Nd ₂ O ₃ B ₂ O ₃	3Sm ₂ O ₃ B ₂ O ₃	3Eu ₂ O ₃ B ₂ O ₃
B ¹⁰	B ¹¹				
		1385w	1385w	1386w	1386mb
				1325wsh	1325sbsh
1338msh	1296msh	1310msh	1308msh	1277svb	1279svb
1292s	1250svb	1262svb	1267svb	1242svb	
1272ssh	1230sbsh	1240sb	1238svb	1200svb	
1225svb	1182svb	1180svb	1194svb	1177svb	
				999sb	1177svb
				969sb	
938m	937m	945m	971m		
		920w			
		903m		910vw	904m
					832sb
		778m	847w		768m
			780m		767w
					752msh
					743msh
					734msh
					707s
					682mb
					598s
					550sb
781s	753s	751s	750s	751s	
		749s		747s	
767w	739vw			740s	
				726s	
732sb	713sb	713sb	727s	715s	
			646m	650m	767s
					688msh
609m	606m	607bsh		587m	622mb
590m	588msh	580mb			596s
559m	576m		582mb		542sb

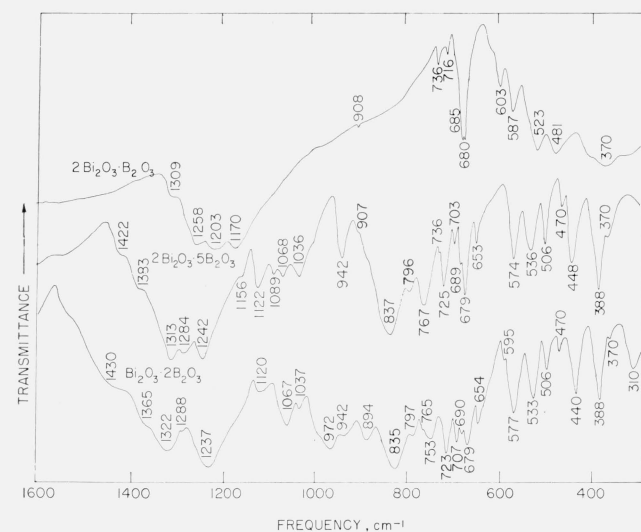


FIGURE 18. Absorption spectra of bismuth borates.

numerous bands which are nearly coincident in the different compounds. It was suspected that these bands might arise, in part from bismuth oxide impurities or from Bi—O bond modes. However, the pure oxide itself shows no absorption spectrum in this frequency range. The spectrum of the 2:1 compound is surprisingly simple and gives evidence of boron only in 3-fold coordination. The absence of strong bands just above 700 cm⁻¹ (the ν_2 region for trigonal ions) and the apparent presence of modes derived from ν_2 at 685 cm⁻¹ and 680 cm⁻¹ may be taken to indicate that the anion is a complex polymer of trigonal BO₃ groups. The occurrence of low frequency bands supports this idea. Because of the simplicity of the spectrum it is probable that a highly symmetrical ion is present. The other bis-

TABLE 18. Infrared absorption spectra of the 3:1 rare earth borates—Continued

(cm ⁻¹)					
3Gd ₂ O ₃ B ₂ O ₃	3Tb ₂ O ₃ B ₂ O ₃	3Dy ₂ O ₃ B ₂ O ₃	3Ho ₂ O ₃ B ₂ O ₃	3Er ₂ O ₃ B ₂ O ₃	3Tm ₂ O ₃ B ₂ O ₃
1392wb	1385w	1385w	1385w	1385w	1385vwsh
1325sbsh	1335sbsh	1344msh	1349msh	1352msh	1355msh
	1295sb	1300sb	1305sb	1302sb	1310sb
1280svb		1272ssh	1277msh	1270msh	
	1220sbsh	1228ssh		1265msh	1272mb
			1232ssh	1232sb	1242sb
1180svb	1180svb	1185sb	1197sb	1194sb	1212sb
	1045svb	1045ssh			
			1047ssh	1050ssh	1055ssh
					1032ssh
998sb	1008sb	1008msh			
968sb	982sb	986s	994sb	1000sb	1012sb
		940m	942m	945m	950sb
		920w	922w	925m	932m
905m	910sb	912w	914wsh		
830sb	840sb	840sb	849sb	850sb	858sb
		788wb	782wb	790wb	
770m	770m	772msh	770msh	770msh	770msh
767w		735sbsh	741ssh	748s	758s
752msh					750s
743msh					
734msh					
707s	723s	723s	723s	722s	721s
682mb	708s	708s	709s	707s	708s
	680wb				
		636mb	637m	641mb	647mb
	600w	602m	603m	605m	
		557m	557sb	567sb	567sb

TABLE 19. Infrared absorption spectra of the bismuth borates (cm⁻¹)

2Bi ₂ O ₃ ·B ₂ O ₃	3Bi ₂ O ₃ ·5B ₂ O ₃	Bi ₂ O ₃ ·3B ₂ O ₃	Bi ₂ O ₃ ·4B ₂ O ₃
	1422msh	1430bsh	1448svb
	1383msh		1376svb
1309msh	1313sb	1365bsh	
	1284sb	1322sb	
1258sh	1242sb	1288bsh	
1203sb		1237vsb	1238svb
1170sb			1191ssh
	1156msh		1130msh
	1122sb	1120mb	
	1089s		
	1068sb	1067sb	1074sb
	1036sb	1037sb	
		972svb	
908w	942sb	942m	930msh
	907wsh	894mb	890svb
	837svb	835svb	835svb
	796m	797m	
	767s	765m	
		753m	750s
736m	736wsh		
716m	725s	723s	722s
	703m	707m	
685s	689m	690w	689mb
680s	679s	679s	
	655m	654m	653w
			623w
603sb			595msh
578sb	574s	577s	579s
	536s	533s	529s
523sb			
	506s	506s	503s
481svb			
	470m	470w	470w
	448s	440s	436sb
	388s	388s	389sb
370sb	370ssh	370ssh	
		310sb	

muth borates show evidence of polymeric anions containing both 3-fold and 4-fold coordinated boron. It is apparent from the many points of similarity that the anions are very closely related in the 3:5, 1:3, and 1:4 compounds. Furthermore, the spectrum of the 1:3 bismuth borate is quite similar (but not identical) with the spectra of the 1:3 rare earth borates, and all the bismuth borate compounds except the 2:1 compound show spectra with marked

resemblances to the spectra the other metal borates that have high proportions of B_2O_3 .

c. Odd Borates

Several borates are formed in systems already discussed in apparent odd ratios of metal oxide to boric oxide. These spectra are given here, together with those of compounds of doubtful composition. Representative spectra are not shown but the observed absorption bands are given in table 20. No detailed discussion of these spectra will be attempted. The questions concerning the composition of the 5:2 zinc borate have been noted previously (sec. 6.2.c). The spectrum would be consistent with boron in 3-fold coordination except for the strong band at 940 cm^{-1} which may indicate tetrahedral boron. In the 4:1 lead borate only trigonal boron is indicated. The 3:1 copper borate, whose exact composition is not established, gives indications of only 3-fold coordination of boron as would be expected from the nominal formula. The spectrum shows an interesting series of weak broad bands in the 858 cm^{-1} to 1032 cm^{-1} range which may be indicative of impurities. In the 5:2 zinc borate, the 4:1 lead borate and the 3:1 copper borate the spectra all indicate polymeric anions composed of trigonal BO_3 groups. The 5:4 lead borate spectrum indicates both coordinations of boron and the aluminum borate spectrum is complicated by the possibility of Al—O bond vibrations occurring in this spectral range. The 1:9 cesium borate spectrum shows very strong absorption throughout the range 500 cm^{-1} to 1500 cm^{-1} with no clearly resolved bands. At least a part of the broad absorption may arise from the glassy phase which is known to be present in small amounts. The only clearly recognizable feature of this spectrum consists of a complex group of bands near 460 cm^{-1} .

TABLE 20. Infrared absorption frequencies of "odd" borates (cm^{-1})

5ZnO2B2O3	4PbOB2O3	5PbO4B2O3	3CuOB2O3	9Al2O32B2O3	Cs2O9B2O3
1307svb 1237svb	1329m 1278s 1247s	1292sb	1500m 1480m	1412sb 1390sb	} Very strong broad absorption 1500 cm^{-1} to 600 cm^{-1}
1085sb	1179sb	1232sb 1196m 1132m 1107m	1340sb 1192mb 1152sb	1327sb 1260sb 1230m 1189s 1100mbsh 1025mbsh	
1040mb		1037sb 975sb 927sb 900ssh	1032wb 980wb 942wb 910wb 888wb 858wb	875sb	
991wsh 940svb	972m 891w	820svb		827mbv 798sb 775msh 732s 710msh 693m 669s	
883w 863w	756s 728s	792sb 765sb 750msh 722m	737msh 722s	552sb 524m 493sb 458m 443m 418m	} 505ssh 460sb
715sb	709w 690s 608s	711m 702m 681s 661s 628m 600s	696s 671s 663s 648ssh 611m 594m		
672s					
620mb					
955mb	559s 521m 503m	582s 567msh 560msh	553m		
475s		508s 476s 434s 418s	508s 477s 439ssh 433s		
437s					
415s	408sb 356sb	409s 399s 370s	397s 375s		
377vsb					

d. Borates Containing Only Tetrahedrally Coordinated Boron

The three borates discussed in this section are known to contain boron only in BO_4 groups and consist of the 1:1 compounds of Ta_2O_5 , As_2O_5 , and P_2O_5 with B_2O_3 . The structures are known for all of these compounds which have the empirical formulae ABO_4 with A representing Ta, P, or As. Both PBO_4 and $AsBO_4$ form crystals of space group $S_4^2 \equiv C_2$ [46] and $TaBO_4$, which is isostructural with zircon is of space group D_{19h}^{19} [58]. The latter compound is expected to give a spectrum typical of tetrahedrally coordinated boron with all normal modes active. Coupling with the modes arising from Ta—O bonds is not expected to be important because of the relative weakness of these bonds and the large mass of the Ta atoms. It was determined experimentally that Ta_2O_5 showed no absorption in the frequency range used here. The compounds PBO_4 and $AsBO_4$ both contain two distinct types of tetrahedra, one of which is the BO_4 unit, the other either PO_4 or AsO_4 tetrahedra. The two types of tetrahedra are connected at corners and each oxygen is therefore shared by boron and either phosphorous or arsenic. The P—O and As—O bonds are expected to be similar in strength to the B—O bonds and the infrared spectrum will be expected to be representative of tightly coupled oscillators having at least some fundamentals nearly equal in frequency.

The spectra obtained on these compounds are shown in figure 19 and the observed absorption bands are tabulated in table 21. The spectrum of $Ta_2O_5 \cdot B_2O_3$ shows 3 strong bands at 840 cm^{-1} , 579 cm^{-1} , and 490 cm^{-1} , which have been assigned tentatively as corresponding to ν_3 , ν_1 , and ν_4 , respectively. The missing ν_2 band may be located near 300 cm^{-1} and may correspond to the apparent absorption band observed in figure 19. However, the location of ν_2 or its presence in the spectrum is not certain because of the low energy available near 300 cm^{-1} . The assignments given are plausible and consistent with the expected strengths and complexities of the ν_3 and ν_4 bands. The assignments were not corroborated by isotopic substitution because of the difficulties involved in preparing the tantalum borate but it appears very probable that this spectrum should be characteristic of the isolated borate tetrahedral unit.

Although the spectra of PBO_4 and $AsBO_4$ are very simple in appearance their interpretation is not clear. First it should be noted that all bands in these compounds with one exception (the 858 cm^{-1} band) are very broad and the tabulated data are subject to considerable uncertainty. In addition it is possible that variations of index of refraction of the powdered specimens may produce artifacts in the observed spectra—the 858 cm^{-1} band is suspected in this connection. It should be noted that the normal frequencies of the isolated PO_4^{-3} ion are given as $\nu_1 \approx 980\text{ cm}^{-1}$, $\nu_2 \approx 363\text{ cm}^{-1}$, $\nu_3 \approx 1082\text{ cm}^{-1}$, and $\nu_4 \approx 515\text{ cm}^{-1}$. Comparing these values and those for $TaBO_4$ in table 21 with the observed frequencies for PBO_4 shows no clear correlation. The fact that

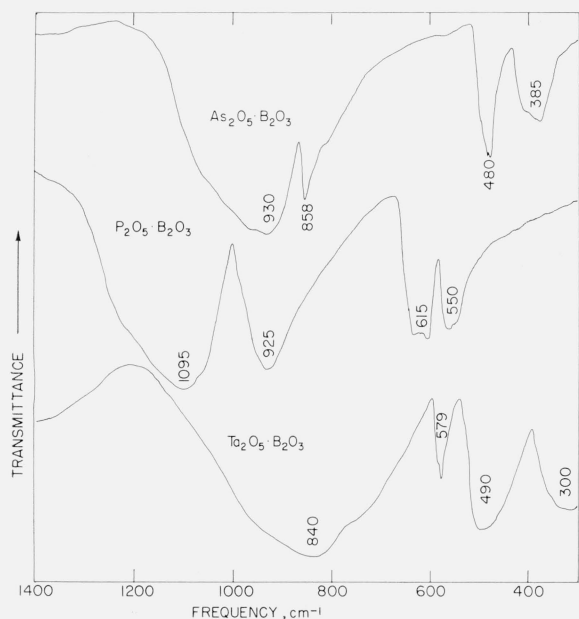


FIGURE 19. Absorption spectra of compounds containing tetrahedrally coordinated boron.

substitution of As for P in the structure produces strong shifts of *all* bands plus the fact that isotopic substitution of boron in a given compound results in shifts which appear to be in unexpected directions forces the conclusion that in a system of such tightly coupled oscillators, individual group frequencies cannot be recognized readily.

TABLE 21. Infrared absorption spectra of compounds containing only tetrahedrally coordinated boron (cm⁻¹)

TaBO ₄	PBO ₄			AsBO ₄
	B ¹¹ & B ¹⁰	B ¹⁰	B ¹¹	B ¹¹ & B ¹⁰
840vsb, ν_3	1095vsb	1065vsb	1085vsb	930vsb
579s, ν_1	925vsb	925vsb	923vsb	858?s
490svb, ν_4	615sb	610sb	617sb	480s
300svb?, ν_2	550sb	535sb	537sb	385sb

7. Spectroscopic Identification of Borate Anions

From the studies described some generalizations on the character of the borate anion can be made on the basis of the observed spectrum. Under normal conditions the spectrum will be complicated by the presence of B¹⁰ and B¹¹ isotopes in their natural abundance and recognition of the weaker, higher frequency bands arising from the B¹⁰ isotope is essential for purposes of identification.

As regards the problem of coordination of the boron, it can be concluded that the group frequency correlations may have certain validity in the spectra of the borates, regardless of the exact structure of the anion. Characteristic bands may shift by as much

as 100 cm⁻¹ or more depending on the structure so that conclusions must be made with caution particularly when very complex anions are involved.

With these reservations in mind, it can be concluded that boron in 3-fold coordination is characterized by the presence of strong, broad absorption in the region 1100 cm⁻¹ to 1300 cm⁻¹. This band (or more generally bands) is one of the strongest and most prominent features of the spectrum. In addition there is always absorption in the 700 cm⁻¹ to 780 cm⁻¹ region (derived from ν_2 of the trigonal ion) which is strong, usually sharp, and frequently (but by no means always) consists of a single band. Both of these characteristic bands are strongly dependent on isotope mass and isotopic substitution can be used to differentiate the desired bands from others which occur in the same frequency region.

Boron in 4-fold coordination can be determined with much less certainty, particularly when boron in 3-fold coordination is also present. Based on the present (and previous work) it may be concluded that the most characteristic feature is the presence of strong, broad absorption in the 800 cm⁻¹ to 1100 cm⁻¹ region. This band (or bands) is very strong and broad and its position is strongly sensitive to isotope mass. Absorption in the 600 cm⁻¹ to 800 cm⁻¹ region can be distinguished from the absorption of boron in 3-fold coordination by the fact that it is relatively insensitive to isotopic mass. Caution must be exercised in this case to recognize overtones and combination bands which may be found in the region above 1100 cm⁻¹ and be mistaken for fundamentals of trigonal borate groups. Overtones and combinations may be strongly dependent on isotope mass but may be differentiated from the fundamentals by their relative weakness compared to the fundamental bands. It appears to be characteristic of tetrahedral borates that reasonably strong absorption bands are found at much lower frequencies than in the trigonal borates (for example a band is generally observed near 470 cm⁻¹ which may be derived from ν_4) but this observation is of little diagnostic value. Complex borate anions give rise to a large number of low frequency modes so that the tetrahedral boron bands, if present, cannot be identified with assurance.

The identity of individual anions can be determined with assurance in a limited number of cases only. The best identification can be made in the case of the planar BO₃ group. This spectrum is defined by the strong absorption above 1100 cm⁻¹ which may be split into two bands, a strong band in the 700 cm⁻¹ to 800 cm⁻¹ region, and one or two weaker bands below 700 cm⁻¹. A weak sharp band near 1000 cm⁻¹ may appear (see figs. 1 and 2).

The pyroborate ion can probably be recognized from its spectrum. In this case the diagnostic region appears to be the 600 cm⁻¹ to 800 cm⁻¹ region which exhibits three strong bands (see fig. 10). Additional bands may appear slightly above 800 cm⁻¹ but they are much weaker. A sharp moderately strong band will also appear near 1000 cm⁻¹. Bands at still higher frequencies will occur but only

the appearance of the strong 3-fold coordination bands above 1100 cm^{-1} is of concern.

Compounds with infinite chains of triangles yield spectra very similar to those of the pyroborates. In the former, however, the bands appear to be broader, more complex in internal structure, and less easily resolved. The band near 1000 cm^{-1} is weak and may not be observed. The strong bands above 1100 cm^{-1} are also present but broader and less readily resolved than in the pyroborates.

Provided the spectrum obtained for TaBO_4 is typical of an isolated tetrahedral BO_4 group, the characteristics appear to be principally in the strong broad band near 840 cm^{-1} and the slightly weaker band near 490 cm^{-1} . The bands near 579 cm^{-1} and 300 cm^{-1} are not considered to be diagnostic features because they may be inactive in many instances.

Any attempt to identify more complex borate anions solely on the basis of their infrared spectra does not appear possible at this time. Spectra containing large numbers of bands, particularly in the region below 600 cm^{-1} may be taken to be indicative of structurally complex anions of low symmetry. Further detailed interpretations can be made only as x-ray structural data become available for more of the borates.

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8. References

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