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Infrared Spectra of the Hydrated Borates

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Infrared absorption spectra of 42 different hydrated borates were obtained in the 2000–300 cm^{-1} range. A few spectra were obtained between 4000 and 2000 cm^{-1}. Most spectra are complex and cannot be interpreted satisfactorily except in the case of the simplest anions. Many correlations between spectra are possible, however, and possible anion types have been deduced. Differentiation between triangular and tetrahedral boron is possible on the basis of the spectra but is less certain than in the case of the anhydrous borates.

Key Words: Hydrated borates, infrared spectra, absorption spectra, borates, boron coordination, borate anions

1. Introduction

A comprehensive survey of the infrared spectra of the crystalline anhydrous inorganic borates was reported recently [1].[1] The spectra were correlated with known structures and predictions of unknown structures were made on the basis of the observed spectra. Two of the predicted anion structures have been verified by subsequent x-ray crystallographic studies [2, 3]. The obvious extension of the studies to include the hydrated borates is the subject of this report.

The hydrated borates have been subjected to a more systematic study than the anhydrous materials, largely as a consequence of their mineralogical occurrence. Miller and Wilkins [4] reported data on eight hydrated borates obtained by the mull technique. Several years later, Takeuchi [5] studied the spectra of 17 borates of which 12 were hydrated. Takeuchi also used the mull technique of sample preparation. Moenke and his coworkers, in a series of papers, [6–13] have presented spectra obtained on approximately 17 hydrated borates using the KBr pellet technique. Akhamanova [14] has reported on seven hydrated borates and Plyusnina and Kharitonov [15] have studied six, with spectra in both cases being obtained using films deposited from isopropyl alcohol on alkali halide plates. The early work by Miller and Wilkins [4] and that of Takeuchi [5] had a lower frequency limit of about 600 cm^{-1} which is too high to obtain some of the known fundamental vibrations of the borate anion. All the more recent studies, however, extend as far as 400 cm^{-1}.

In the present study, infrared spectra were obtained for 42 different hydrated borates. Most specimens were natural minerals but in many instances synthetic materials were also available. Approximately 63 different specimens were studied so that it was possible to determine the reproducibility of the spectra for materials of different origin—a question of importance for natural minerals which may contain infrared active impurities.

2. Experimental Method and Apparatus

Experimental techniques and equipment were similar to those described previously for the anhydrous borates [1]. A double-beam grating spectrometer was used to cover the range 4000–200 cm^{-1}. This range was covered in two steps, 4000–400 cm^{-1} and 2000–200 cm^{-1}. In each case the lower frequency limit imposed by the available energy was higher than the limits given. Most spectra were obtained only in the range 2000–300 cm^{-1} because the fundamentals of the borate anions were known to occur in this range. For these studies powdered films deposited on CsBr plates from a volatile liquid were used. A few spectra in the higher frequency range were obtained to locate the OH fundamental stretching modes. For these studies the spectra were obtained using a mull with perfluorokerosene as the suspending medium. In both cases a blank cell was placed in the reference beam of the spectrometer. The possibility of dehydrating the specimens precluded using dry air in the instrument and considerable care was exercised in the 500–300 cm^{-1}. region. In this range only those bands were considered to originate in the specimen which were not obtained on a comparison spectrum run with no specimen in the beam.

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

Table 1. *Description of samples studied*

Material	Empirical formula	Origin of specimen [a]
Hambergite	$4BeO \cdot B_2O_3 \cdot H_2O$	C 4744
Bandylite	$CuO \cdot CuCl_2 \cdot B_2O_3 \cdot 4H_2O$	105459.
Teepleite	$Na_2O \cdot 2NaCl \cdot B_2O_3 \cdot 4H_2O$	102798.
Pinnoite	$MgO \cdot B_2O_3 \cdot 3H_2O$	C 4488; synthetic $MgO \cdot B_2O_3 \cdot 3H_2O$ (R. C. Erd).
Inyoite	$2CaO \cdot 3B_2O_3 \cdot 13H_2O$	114260; Pacific Coast Borax open pit, Boron, Calif.
Meyerhofferite	$2CaO \cdot 3B_2O_3 \cdot 7H_2O$	96072; Gower Gulch, Death Valley Nat. Monument.
Colemanite	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$	96445; Pacific Coast Borax open pit, Boron, Calif.
Inderite	$2MgO \cdot 3B_2O_3 \cdot 15H_2O$	11462; Pacific Coast Borax open pit, Boron, Calif.
Kurnakovite	$2MgO \cdot 3B_2O_3 \cdot 15H_2O$	R 11023; Pacific Coast Borax open pit, Boron, Calif.
Inderborite	$MgO \cdot CaO \cdot 3B_2O_3 \cdot 11H_2O$	Inder region, USSR.
Hydroboracite	$MgO \cdot CaO \cdot 3B_2O_3 \cdot 6H_2O$	Inder region, USSR (R. C. Erd via H. B. Mason).
Synthetic	$2SrO \cdot 3B_2O_3 \cdot 5H_2O$	Synthetic strontium colemanite (R. C. Erd via C. R. Parkerson).
Tunellite	$SrO \cdot 3B_2O_3 \cdot 4H_2O$	Pacific Coast Borax open pit, Boron, Calif.; synthetic tunellite (R. C. Erd).
Nobleite	$CaO \cdot 3B_2O_3 \cdot 4H_2O$	115278; N. of DeBely mine, Death Valley Nat. Monument, synthetic nobleite (R. C. Erd).
Gowerite	$CaO \cdot 3B_2O_3 \cdot 5H_2O$	115277; Hard Scramble Claim, Death Valley Nat. Monument; synthetic gowerite (R. C. Erd).
Veatchite	$SrO \cdot 3B_2O_3 \cdot 2H_2O$	117214; synthetic veatchite (C. R. Parkerson via R. C. Erd).
Synthetic	$CaO \cdot 3B_2O_3 \cdot 2H_2O$	Synthetic calcium veatchite (C. R. Parkerson via R. C. Erd).
Synthetic	$MgO \cdot 3B_2O_3 \cdot 7\frac{1}{2}H_2O$	Synthetic macallisterite (R. C. Erd).
Synthetic	$MgO \cdot 3B_2O_3 \cdot 5H_2O$	Synthetic aksaite (H. A. Lehmann via R. C. Erd).
Synthetic	$SrO \cdot 3B_2O_3 \cdot 4H_2O$?	Synthetic (C. R. Parkerson via R. C. Erd), possibly a dimorph of tunellite but degree of hydration uncertain.
Ginorite	$2CaO \cdot 7B_2O_3 \cdot 8H_2O$	112966; synthetic ginorite (R. C. Erd).
Strontium Ginorite	$2SrO \cdot 7B_2O_3 \cdot 8H_2O$	Natural mineral via R. C. Erd.
Synthetic	$2SrO \cdot 7B_2O_3 \cdot 8H_2O$	Synthetic volkovite [?] (R. C. Erd).
Priceite	$4CaO \cdot 5B_2O_3 \cdot 7H_2O$	Death Valley Nat. Monument (J. F. McAllister via R. C. Erd).
Pandermite	$4CaO \cdot 5B_2O_3 \cdot 7H_2O$	Panderma, Asia Minor (W. T. Schaller via R. C. Erd).
Tertschite	$4CaO \cdot 5B_2O_3 \cdot 20H_2O$[?]	Kurtpinari mine, Bigadic district, Turkey (H. Meixner via R. C. Erd).
Preobrazhenskite	$3MgO \cdot 5B_2O_3 \cdot 4\frac{1}{2}H_2O$[?]	Inder region, USSR (M. E. Mrose via R. C. Erd).
Ulexite	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$	96994; Pacific Coast Borax open pit, Boron, Calif.; Mudd mine, Boron, Calif.
Probertite	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 10H_2O$	96077; Mudd mine, Boron, Calif.; Harmony Borax Works, Death Valley Nat. Monument.
Kaliborite	$K_2O \cdot 4MgO \cdot 11B_2O_3 \cdot 9H_2O$	R 5644.
Parahilgardite	$6CaO \cdot 2CaCl_2 \cdot 9B_2O_3 \cdot 4H_2O$	105822.
Kernite	$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$	95737; Mudd mine, Boron, Cal.
Tincalconite	$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$	107397.
Synthetic	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	Synthetic borax, reagent grade.
Synthetic	$K_2O \cdot 2B_2O_3 \cdot 4H_2O$	Reagent grade.
Synthetic	$Na_2O \cdot 5B_2O_3 \cdot 10H_2O$	Synthetic (V. Morgan via R. C. Erd).
Larderellite	$NH_4 \cdot 5B_2O_3 \cdot 4H_2O$	C 4481.
Ammonioborite	$NH_4 \cdot 5B_2O_3 \cdot 5\frac{1}{3}H_2O$	R 6167.
Ezcurrite	$2Na_2O \cdot 5B_2O_3 \cdot 7H_2O$	Tincalayu, Argentina.
Synthetic	$2Na_2O \cdot 5B_2O_3 \cdot 7H_2O$	N. P. Nies via R. C. Erd.
Synthetic	$2Na_2O \cdot 5B_2O_3 \cdot 5H_2O$	N. P. Nies via R. C. Erd.
Synthetic	$2Na_2O \cdot 5B_2O_3 \cdot 4H_2O$	C. Cipriani via R. C. Erd.
Szaibelyite	$2MgO \cdot B_2O_3 \cdot H_2O$	95111.
Sussexite	$2MnO \cdot B_2O_3 \cdot H_2O$	C 4456.
Synthetic	$NaBO_3 \cdot 4H_2O$	Sodium perborate.

[a] Number of specimens studied is equal to the number of listings for each material separated by semicolons. Numerals represent catalog numbers in the mineral collection of the Smithsonian Institution.

3. Samples

The samples studied are listed in table 1. Column 1 of this table lists the mineral or chemical name, column 2, the empirical formula, and column 3, the source of the material. Throughout this paper, samples will be referred to by the mineral names and synthetic samples will be designated by their composition unless it is known that the synthetic and natural minerals are equivalent. In the latter case the mineral name will be used. Samples were obtained generally from two sources, the mineralogical collection of the Smithsonian Institution and the U.S. Geological Survey. In column 3, designations denoted by numbers correspond to catalog numbers in the Smithsonian collection. Origins of specimens obtained from the U.S. Geological Survey are listed in column 3. The total number of samples of each mineral type studied is indicated by the number of listings in column 3 separated by semicolons. The order in which the samples are listed in table 1 corresponds to the order followed in the discussion.

4. Results and Discussion

4.1. Presentation of Data

Data will be presented here as in the previous report [1]. Compounds are grouped according to the anion type expected based on the ideas presented by Christ [16]. For each compound, observed bands are tabulated with the type of band designated by the usual abbreviations.[2] Typical spectra are shown only for a few of the materials and only for the range 1800 cm⁻¹ to approximately 300 cm⁻¹.

4.2. Borates With Simple Anions

In order to assess the extent to which analyses of the spectra of the hydrated borates can be pursued, it is instructive to consider first the spectra of hambergite, bandylite, teepleite, and pinnoite. These materials have known structures with relatively simple anions. Hambergite contains unhydrated planar BO_3^{-3} groups [17, 18] and the formula $Be_2(OH)BO_3$ represents the structure. Both bandylite and teepleite contain isolated $B(OH)_4^{-1}$ groups and their structures may be represented by the formulas $CuB(OH)_4Cl$ and $Na_2B(OH)_4Cl$ respectively [19, 20, 21]. Pinnoite contains anions of the form $[B(OH)_3OB(OH)_3]^{-2}$ which can be considered as resulting from condensing two $B(OH)_4^{-1}$ groups with the elimination of H_2O [22]. It is of interest to compare the spectra of these substances with those obtained in previous studies of the anhydrous borates [1] where it was found that boron in

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[2] s = strong, v = very, b = broad, m = medium, w = weak, sh = shoulder.

three-fold coordination could be differentiated by the strong absorption derived from ν_3 of the isolated ions which generally persisted in the complex anion. It was found that triangular boron even in complex anions exhibited broad strong absorption in the region 1100–1300 cm^{-1} and tetrahedral boron in the region 800–1100 cm^{-1}. The ν_2 and ν_4 region (600–800 cm^{-1}) of the isolated ions also was found useful for differentiating these anion types provided isotope substitution was possible (see ref. 1; figs. 1, 2, 19, and p. 486).

The validity of these conclusions with respect to the hydrated borates can be evaluated by considering the spectra of the hydrates with simple anions shown in figure 1 and the absorption bands listed in table 2. In hambergite the strong band at 1300 cm^{-1} can be ascribed to ν_3 and the strong broad band centered at 750 cm^{-1} probably arises from Be–O vibrations. The 600 and 650 cm^{-1} bands superimposed on the Be–O band are probably the two components of ν_4, and ν_2 is probably obscured by the Be–O band. The 1155 cm^{-1} band is unexpected. It does not seem strong enough for a ν_3 band and it is tentatively considered to be a bending mode involving BeOH.

In teepleite and bandylite the ν_3 bands are ascribed to the strong bands between 900 and 950 cm^{-1}. The somewhat weaker band at 845 cm^{-1} in teepleite may arise from a second component of ν_3 or from ν_1. In both materials the strong bands at lower frequencies may be due to ν_4 or to an OH torsional mode. In teepleite the bands at 1170 and 1302 cm^{-1} are quite strong and might be erroneously considered to be ν_3 fundamentals of triangular borate ions. In this spectrum they are weaker than the ν_3 for the tetrahedral borate group and there is no danger of misinterpretation. These bands may represent either combinations or B–OH bending modes. In bandylite the 1255 cm^{-1} band is no weaker than the ν_3 band and misinterpretation is possible. From spectral studies on orthoboric acid, however, it seems that this band most probably arises from an OH distortion vibration [23].

In the pinnoite spectrum the strong broad bands in the 800–1000 cm^{-1} range are the most prominent features of the spectrum and presumably are derived from the antisymmetrical vibration, ν_3, of the tetrahedral units. The complex series of bands below 800 cm^{-1} are probably derived from the original ν_2 and ν_4 vibrations. The region above 1100 cm^{-1} contains three broad strong bands which are somewhat weaker than the antisymmetrical bands and are probably the result of B–OH distortion modes. These bands might easily be assumed to arise from triangular boron in a material with an unknown anion and show that interpretations must be made with great caution.

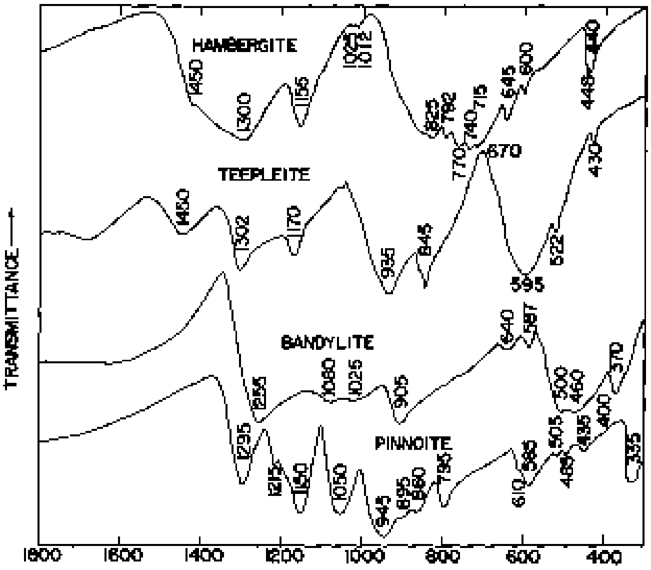


FIGURE 1. *Infrared absorption spectra of hydrated borates containing simple anions.*

TABLE 2. *Infrared absorption spectra of borates with simple anions*

Hambergite	Pinnoite	Teepleite	Bandylite
	3560 s	3530 s	3480 s
	3400 sb	3400–2500 sh	3440 sbsh
	3140 svb	1450 mvb	2900 sb
1450 ssh	2930 vb	1302 sb	1255 svb
1300 vsvb	1295 sb	1170 s	1080 mvb
	1215 mb	935 vsb	1025 mvb
1155 s	1150 sb	845 vs	905 ssb
1025 w	1050 svb	670 sh	640 w
1012 w	945 svb	595 svb	587 w
	895 msh		
825 sb	800 sb	522 w	500 svb
792 s	795 sb	430 w	460 svb
770 s			370 m
740 s			300 w
715 s	610 wsh		
645 m	585 mb		
600 m	505 w		
448 m	485 m		
440 m	435 mb		
	400 m		
	335 m		
	310 m		

On the basis of these spectra it must be concluded that hydration of the borate anions produces spectra which cannot be interpreted readily from a knowledge of the spectra of the corresponding anhydrous anion. Hydration appears to produce absorption bands, some of which are very strong, throughout the spectra range studied. Bands apparently derived from ν_3 modes of the anhydrous BO_3^{-3} and BO_4^{-5} groups still appear in the spectra of the hydrated anions. These bands are very strong and occur in the expected positions, i.e., 800–1100 cm^{-1} for tetrahedral boron and above 1100 cm^{-1} for triangular boron. However, strong bands apparently originating from B–OH distortion modes complicate the spectra, particularly in the region 1100–1400 cm^{-1}.

Data on teepleite have been obtained by Plyusnina and Kharitonov [15]. In gross features the spectra agree reasonably well but there are significant differences. For example, they do not report the 1450 or 430 cm^{-1} bands at all and band positions vary up to 21 cm^{-1} for the 845 cm^{-1} band which they found at 866 cm^{-1}. The spectrum of pinnoite has been reported by Takeuchi [5] with considerable disagreement in the data. Comparison of the various spectra shows that there are considerable discrepancies in numbers of bands, band locations, and band contours.

5. Divalent Metal Borates

5.1. The $MeO \cdot 3B_2O_3 \cdot xH_2O$ Compounds

The family of divalent metal borates of general formula $2MeO \cdot 3B_2O_3 \cdot xH_2O$ comprise the minerals inyoite, meyerhofferite, colemanite, fabianite, inderite, kurnakovite, inderborite, and hydroboracite. Except for fabianite (2 · 3 · 1) all of these minerals, as well as a synthetic strontium (2·3·5) analog of colemanite were examined during the present study. The infrared spectrum for fabianite has been reported by Kuhn and Moenke [13]. Among the other 2·3·x compounds crystal structures have been determined for the following: Inyoite [25], meyerhofferite [26], colemanite [27], inderite [28, 29], and hydroboracite [30]. These borates all contain similar anions built up from six-membered rings formed from alternate boron and oxygen atoms by corner sharing among two BO_4 tetrahedra and one BO_3 triangle. The oxygen atoms not shared by two boron atoms attach a hydrogen to form hydroxyl groups [16]. Isolated anions, $[B_3O_3 \cdot (OH)_5]^{-2}$ are found in inyoite, meyerhofferite and inderite. In colemanite and hydroboracite, similar anions polymerize into chains having the formula $[B_3O_4(OH)_3]_n^{-2n}$.

Typical spectra for some of these materials are shown in figure 2 and the observed absorption bands are listed in table 3. As seen in figure 2, the spectra are very complex and more than a cursory interpretation is not possible. The spectra of inyoite and meyerhofferite are very similar with the predominant features being a strong complex absorption band near 1400 cm^{-1} and a similar band below 1200 cm^{-1}. The former band probably is the counterpart of the antisymmetric mode for the triangular boron atoms and the latter band for the tetrahedral boron groups.

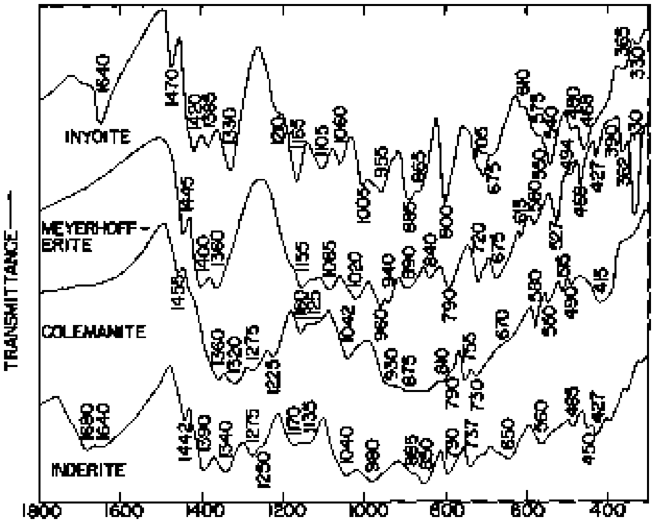


Figure 2. *Infrared absorption spectra of* $2MeO \cdot 3B_2O_3 \cdot XH_2O$ *compounds.*

Table 3. *Infrared absorption spectra of* $2MeO \cdot 3B_2O_3 \cdot XH_2O$ *compounds*

Inyoite	Kurnakovite	Inderite	Inderborite
3530 s	3550 m		
3440 s	3450 s		
3200 vsb	3200 svb		
		1680 mb	
1640 mb	1650 mvb	1640 mb	1660 mvb
1470 msh	1450 msb	1442 msh	1460 msh
1420 s	1400 sb		1410 sb
1385 s	1390 s	1390 sb	1390 msh
1330 s	1347 sb	1340 sb	1340 sb
	1257 s	1275 s	1290 msh
1210 msb	1215 s	1250 msh	1200 sb
1165 s	1160 m	1170 mb	1150 wsh
1105 sb	1080 msb	1135 mb	1065 s
1060 s	1045 msb	1040 s	1020 msh
1005 s	1010 sb		
955 sb	987 sb	980 svb	960 sb
885 sb	860 mvb	885 msb	
865 sb		850 sb	860 sb
800 s	807 s	790 m	810 m
	795 m	737 m	755 m
705 sb	710 m		715 mvb
675 msh	650 mb	650 mvb	650 mbsb
610 w			
575 msh		560 m	
550 w	520 mb		530 mvb
540 m			
480 msh		485 m	
468 s	460 s	450 m	435 m
365 m		427 s	
330 w		325 mb	

Table 3. *Infrared absorption spectra of* $2MeO \cdot 3B_2O_3 \cdot XH_2O$ *compounds* – Continued

Colemanite	Sr Colemanite	Hydroboracite	Meyerhofferite
3590 s			3600 s
3510 b			3470 s
			3420 sb
			3000 sb
3130 svb			3020 svb
1455 msh	1450 msh		1445 msh
1360 sb	1350 sb	1365 sb	1400 sb
1320 sb	1300 sb	1300 s	1360 sb
1275 sb	1260 sb	1280 s	
1225 s	1190 mb	1188 s	
1160 mb	1150 mb	1130 mb	1155 sb
1125 mvb	1060 msh	1080 sb	1085 sb
1042 s	1030 mb	1050 mb	1020 sb
		985 mbsh	960 sb
930 svb	925 b	950 sb	940 sb
875 svb	865 sb	882 s	890 mb
810 msb		835 s	840 mb
790 msb	790 msh	800 msb	790 sb
755 s	750 s	760 s	720 s
730 s	730 m		675 m
670 w	710 msh		615 w
580 m	575 m	580 m	580 m
550 m	545 w	550 w	
515 m	510 w	530 w	527 m
490 w	490 w	505 w	494 w
		470 m	468 s
	435 w	435 w	427 m
415 sb		425 w	
		410 w	390 w
			362 m
	330 sb	310 sb	330 s

Aside from the gross similarity it is not possible to correlate the spectra band for band because there appear to be noticeable shifts of bands between the two spectra. These shifts are probably to be attributed to differences in hydrogen bonding largely produced by water molecules in the two structures, the formula of inyoite having $4H_2O$ whereas that of meyerhofferite has only one H_2O (table 1). The noticeable effects throughout the spectral range produced by this water are the main deterrent to a more detailed analysis of these spectra. The effect of polymerization on the isolated anions to form the chains in colemanite and hydroboracite can be determined by comparing their spectra with those of inyoite and meyerhofferite. The bands in colemanite and hydroboracite are broader and apparently more complex. In addition, there is a considerable apparent shifting of bands as might be expected from loss of hydrogen bonding water and coupling of the anions. The spectrum of colemanite gives a clear indication that the stretching vibrations involving the triangular boron atoms are represented by the band complex near 1300 cm^{-1}. In the spectra of inyoite and meyerhofferite the strong bands, just below 1200 cm^{-1} might have been considered part of the antisymmetric stretch of the triangular borons. The fact that these bands become much weaker in colemanite which contains fewer B–OH bonds implies that these bands may arise from B–OH bending modes which might be expected in this frequency range [23]. It should be noted, however, that the spectrum of fabianite reported by Kühn and Moenke [13] appears to contradict the present conclusions, because it exhibits a strong band near 1142 cm^{-1}.

Inderite and kurnakovite are polymorphs and their spectra correspond very closely as shown by the tabulated bands. Inderborite, a mixed calcium-magnesium compound, also shows a spectrum similar to both the magnesium and the calcium compounds. The gross features of the spectra of the various magnesium and calcium compounds are also similar, but there are many differences in band positions and intensities.

Data on all of these materials, except the synthetic compound, have been reported by one or more of the earlier workers [5, 7, 8, 9, 14, 15]. In place of comparing the previous data for each material, it is useful to consider reported results on colemanite which has been studied by all these investigators. The frequency range considered is from 650 to 1350 cm^{-1} since this was the range used by Takeuchi [5]. In general appearance, of all five spectra for colemanite are very similar, but the similarity holds only for the gross features. Between 650 and 1350 cm^{-1} Takeuchi [5] and Moenke [7] report twelve absorption bands; Plyusnina and Kharitonov [15], fourteen; Akhamanova [14], nine; and the present work, thirteen. Thus the most probable number of bands would seem to be between twelve and fourteen. However, the totals are obtained quite differently by the several workers. Consider, for example, the 1042 cm^{-1} band of figure 2 which appears to be distinct and well separated from neighboring bands. Akhamanova [14] reports a band at 1050 cm^{-1}, Plyusnina and Kharitonov [15] a strong band at 1048 cm^{-1} plus two additional bands at 1002 and 1062 cm^{-1}. Moenke [7] a strong band at 1046 cm^{-1} and Takeuchi's [5] spectra indicate a band at about 1030 cm^{-1}. In addition to these uncertainties in band numbers and locations there are considerable differences in relative intensities and band contours for many of the bands throughout the spectrum. The same considerations apply to comparisons between the present and previous data on the other members of the 2:3:x borates. Possible explanations and implications of these facts will be discussed later.

5.2. The $MeO \cdot 3B_2O_3 \cdot XH_2O$ Compounds

Compounds studied with the empirical formula $MeO \cdot 3B_2O_3 \cdot XH_2O$ are tunellite, nobleite, gowerite, synthetic aksaite, veatchite, synthetic calcium-veatchite [32], synthetic macallisterite [33], and a synthetic 1:3:4? strontium borate. Of these materials, the structure is known only for nobleite and tunellite [34] which are isomorphous. The anion consists of three six-membered rings forming a $[B_6O_9(OH)_2]^{-2}$ unit. The six-membered rings are the same as those found in the $2MeO \cdot 3B_2O_3 \cdot XH_2O$ compounds and each contains two tetrahedral and one triangular boron. The $[B_6O_9(OH)_2]^{-2}$ ion contains three triangular and three tetrahedral boron groups and is unique in that one oxygen atom is common to all three rings. The ions are linked in sheets through certain of the off-ring oxygen atoms. The structures of the anions in the other members of this series are not yet known, but it might be expected to be similar, probably linked with differing degrees of hydration and/or polymerization [16].

Data obtained on these materials are given in table 4 and typical spectra are shown in figure 3. It would be expected that these spectra should show some similarities with those of figure 2, since the anions are built of similar units and indeed there are many similarities in band positions in the two sets of spectra. However, it was surmised that the coupling between rings in tunellite would be strong enough to produce considerable broadening and band overlap. The reverse situation actually occurs, many bands being clearly resolved and relatively sharp. From the similarities of the spectra (see data of table 4), it is clear that nobleite, tunellite, and the synthetic 1:3:4? synthetic strontium borate have similar anions. Examination of figure 3, shows that it is probable that gowerite has the same anion on the basis of the similarity of the spectra. In gowerite the bands are sharper and appear to be resolved better, a result to be expected if depolymerization of the anion occurs with increased water content. It also appears that veatchite possesses the same anion as tunellite with band broadening and loss of resolution accompanying

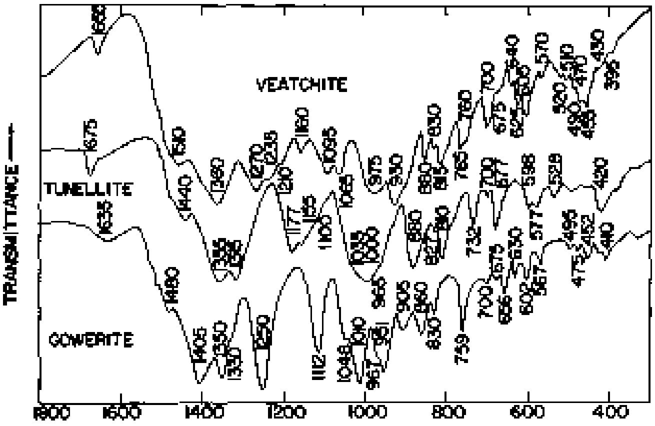


FIGURE 3. *Infrared absorption spectra of* $MeO \cdot 3B_2O_3 \cdot XH_2O$ *compounds.*

the dehydration and polymerization. From the tabular data (table 4), it is clear that the spectra of veatchite and synthetic calcium-veatchite are very similar and the materials probably contain the same anion. The conclusions with respect to the two magnesium compounds, synthetic aksaite, and synthetic macallisterite, are made with much less certainty; but again it seems probable that these materials also may contain the same anion with differing degrees of hydration and polymeriztion. On the basis of the infrared spectra alone, therefore, it is concluded that all the $MeO \cdot 3B_2O_3 \cdot XH_2O$ compounds probably contain similar anions. These spectra do not appear to have been reported previously.

TABLE 4. *Infrared absorption spectra of* $MeO \cdot 3B_2O_3 \cdot XH_2O$ *compounds*

Nobleite	Tunellite	Synthetic $SrO \cdot 3B_2O_3 \cdot 4H_2O$?
3540 mb		
3380 svb		
3200 svb		
2900 svb		
1675 mvb	1675 mb	
	1440 msh	1460 mb
1385 sbsh	1355 sb	1375 svb
1322 sb	1315 sb	1325 svb
1300 msh		
1180 mb	1177 mb	1180 sb
1160 mb	1155 mb	
1125 mb		1125 sb
1107 m	1100 w	1100 w
1033 msh	1035 msb	1010 sb
965 sb	1000 sb	962 svb
930 msh	965 msh	927 mb
880 sb	880 sb	875 sb
827 m	827 msh	
806 sb	810 s	810 sb
737 m	732 m	735 m
705 m	700 w	
670 mb	677 m	670 mb
602 m	598 m	
570 w	577 m	
	528 w	
460 wb		
425 w	420 m	

TABLE 4. *Infrared absorption spectra of* $MeO \cdot 3B_2O_3 \cdot XH_2O$ *compounds*—Continued

Veatchite	Synthetic Ca-Veatchite
3420–2900 b	
1655 w	1665 w
1510 msh	
1360 sb	1390 sb
1270 sb	1265 wsh
1235 msb	1240 sb
1210 wsh	
1160 m	1180 msh
1095 mb	1130 m
1065 mb	1075 mb
975 sb	975 sb
930 sb	910 sb
880 m	870 m
830 w	832 m
815 m	810 m
765 m	755 m
760 m	745 wsh
700 m	700 w
675 msb	
640 w	650 w
625 m	610 m
606 m	600 wsh
570 w	572 wsh
520 w	535 wb
510 w	
490 w	495 w
470 m	
455 m	
430 msh	
395 mb	

TABLE 4. *Infrared absorption spectra of* $MeO \cdot 3B_2O_3 \cdot XH_2O$ *compounds*—Continued

Gowerite	Synthetic Aksaite	Synthetic MacAllisterite
	3600 s	
	3450–2400 sb	
1635 wb	1652 mb	
1480 msh	1485 msh	1470 msh
1405 s	1425 sb	1410 sb
1350 s	1385 sb	1358 sb
1330 msh	1325 sb	
1250 s	1245 sb	1240 s
	1210 sb	
1112 s	1155 mb	1158 mb
	1095 sb	1122 sb
1048 ssh		1060 sb
1010 s	1020 sb	1005 msh
		980 m
967 msh		965 m
951 s	950 sb	880 msh
905 mb	898 mb	
860 mb	850 mb	855 s
830 m		812 s
759 m	800 sb	
700 w	725 w	698 wb
675 w	675 mb	670 m
656 m	655 w	
630 w		
602 w		
567 w	535 w	480 wb
495 w	455 w	
475 w		
452 w		
410 w	410 w	440 w

5.3. The $2MeO \cdot 7B_2O_3 \cdot 8H_2O$ Compounds

Three members of this series were studied, the data are given in table 5 and spectra are shown in figure 4. The marked similarity of the spectra and the compounds makes it almost certain that the anions are identical. The structures of the anions are not known and the spectra are too complex to attempt to predict the anion on this basis alone. There is no doubt that the anion contains both three-fold and four-fold coordinated boron as shown by the strong bands

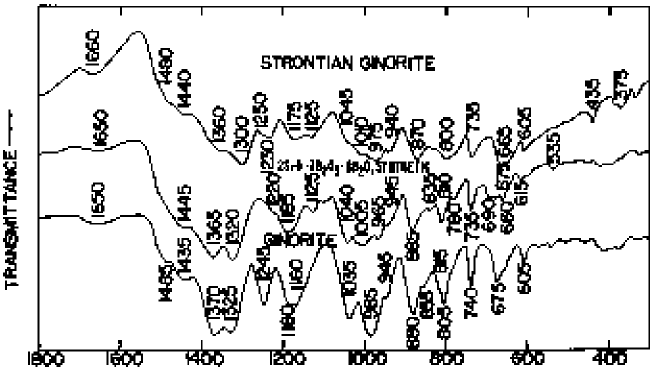


FIGURE 4. *Infrared absorption spectra of* 2MeO · $7B_2O_3$ · $8H_2O$ *compounds.*

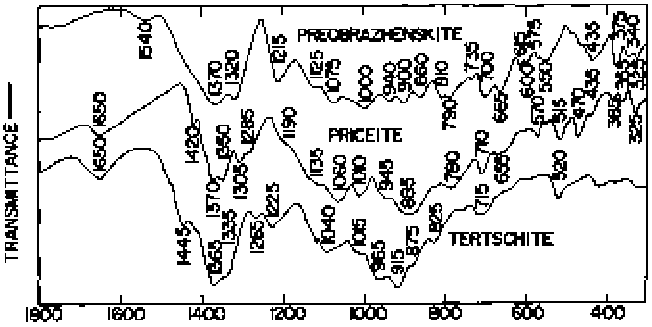


FIGURE 5. *Infrared absorption spectra of miscellaneous hydrated divalent metal borates.*

TABLE 5. *Infrared absorption spectra of* 2MeO · $7B_2O_3$ · $8H_2O$ *compounds*

Ginorite	Strontian Ginorite	2SrO · $7B_2O_3$ · $8H_2O$ Synthetic
3230 vvvb		
1650 wvb	1660 mvb	1650 wvb
1485 msh	1480 mbsh	
1435 msh	1440 mbsh	1445 mbsh
1370 s	1360 svb	1365 s
1325 s	1300 sb	1320 s
1245 s	1250 m	
	1230 mb	1220 mb
1180 s	1175 svb	1185 s
1160 s	1125 mvb	1125 m
1035 m	1045 m	1040 s
985 sb	1010 sb	1005 sb
945 m	975 svb	965 m
880 s	940 sb	945 msh
855 msb	870 s	885 s
815 msh		835 m
805 s	800 sb	810 s
		780 msh
740 s	755 s	735 s
675 sb	655 sb	690 m
605 m	605 m	675 m
		660 m
	435 m	615 w
	375 mvb	535 w

TABLE 6. *Infrared absorption spectra of miscellaneous divalent metal borate compounds*

Priceite	Tertschite	Preobrazhenskite
1650 mvb	1650 mb	1540 mvb
1420 m	1445 m	
1370 s	1365 s	1370 sb
1350 s	1335 ssb	1320 s
1305 s		
1285 msh	1265 w	
1190 msh	1225 m	1215 sb
1135 msh		1125 msb
1060 sb	1040 sb	1075 sb
1010 sb	1015 msh	1000 svb
945 ssh	965 sb	940 mb
885 svb	915 sb	900 m
	875 msh	
780 sb	825 m	860 mvb
710 m	715 m	810 m
655 mb		790 m
		735 w
570 m		700 sb
515 m	520 m	665 mb
470 m		615 m
		600 w
435 w		575 w
		550 mb
385 m		435 mvb
355 w		375 m
325 m		340 m
		325 m

near 1400 and 1000 cm^{-1} respectively. In addition the spectra show a strong resemblance to the previous spectra for compounds containing six-membered rings of alternate boron and oxygen atoms, with one triangular and two tetrahedral boron atoms. Consequently, it appears likely that these rings may exist in the anions. The relative weakness of lower frequency vibrations (i.e., below 600 cm^{-1}) in these spectra, however, is an indication that the anions are not coupled six-membered rings and it is very unlikely that the anions are so small that no low frequency vibrations exist. It is probable that the symmetry of the anions is sufficiently high that lower frequency modes are much weaker than in the previous compounds. Again there do not appear to be any previous reports of spectra of these materials.

5.4. Miscellaneous Divalent Metal Borates

Data on the 4CaO · $5B_2O_3$ · XH_2O compounds are given in table 6 together with those for preobrazhenskite — 3MgO · $5B_2O_3$ · $4\frac{1}{2}H_2O$[?] [35]. The spectra are shown in figure 5. The three materials show evidence of both triangular and tetrahedral boron in the strong bands in the 1300–1400 cm^{-1} and 800–1000 cm^{-1} region respectively. The spectra of priceite and tertschite are very similar and these materials may contain similar anions. The spectrum of preobrazhenskite is indicative of a large anion with considerable interaction between the anion structural units.

From the data obtained here the spectra of pandermite and priceite are considered to be identical. The sample of priceite yielded much the better spectrum of the two specimens, that for pandermite being less well resolved. However, for each band found in the spectrum of pandermite a corresponding band is observed in the priceite with frequencies differing at most by ±1 cm^{-1}. In addition, the same relative intensity relationships are shown by the bands in the two materials. It seems possible to conclude that these materials are most probably identical [36].

The spectrum of priceite (pandermite) has been reported by other workers [5, 7, 14, 15] and that of tertschite by Meixner and Moenke [12]. Comparison of the present and previous results leads to the same conclusions mentioned earlier. The spectra for a given material are in superficial agreement. There are many discrepancies when details are examined.

Data obtained on other divalent metal borates are given in table 7 with spectra for ulexite and kaliborite shown in figure 6. The anions of probertite and ulexite are known to be a ring structure containing three tetrahedra and two triangles with one tetrahedron being common to both rings [37, 38]. From the tabulated data it is clear that the infrared spectra corroborate the similarity of the anions in these materials probertite and ulexite. The spectrum of kaliborite is very poorly resolved in the ν_3 region for tetrahedral borate groups, but is otherwise similar to the spectra of ulexite. The parahilgardite yielded a very poor spectrum and it is suspected that this material was contaminated with $CaCO_3$ as the 875 and 725 cm^{-1} bands strongly resemble the ν_2 and ν_4 bands of calcite.

Table 7. *Infrared absorption spectra of miscellaneous borate compounds*

Ulexite	Probertite	Kaliborite	Parahilgardite
3562 s	3620 s		
3400 sb	3550 s		
3000 vsvb	3350 vsvb		
1650 mb	1650 mvb		
1620 mb			
1470 m	1470 m		
1415 sb			
1390 s	1425 msb	1410 msh	1425 vsvb
1355 s	1375 s	1350 sb	1350–1000 vsvb
1315 s	1325 sb		
1205 s	1210 m	1185 svb	
1090 ssh	1130 ssh		
1050 sb	1080 sb	1080 sb	
995 s	1040 m	1000–750 svb	
975 s	985 msh		
950 ssh	955 s		
925 msh	930 s		
855 s	900 s		875 s (CaCO$_3$?)
825 ssb	830 s		790 s
790 m	750 m		775
710 m	675 m	705 s	725 s (CaCO$_3$?)
690 m	555 w	655 s	
530 m	515 m	625	
		570 w	
430 mb	440 m	445 vsb	
350 m	380 m		355 vbvs

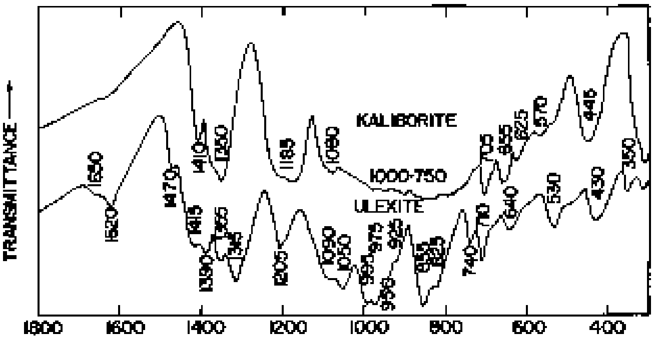


Figure 6. *Infrared absorption spectra of hydrated borates containing both mono- and divalent metal ions.*

6. Monovalent Metal Borates

6.1. The $Me_2O \cdot 2B_2O_3 \cdot XH_2O$ Compounds

Several borates of the type $Me_2O \cdot 2B_2O_3 \cdot XH_2O$ were studied and the data are tabulated in table 8. Typical spectra for tincalconite and potassium tetraborate tetrahydrate are shown in figure 7. Morimoto [39] has determined the structure of borax and found that the anion consists of isolated $[B_4O_5(OH)_4]^{-2}$ rings. Marezio et al., [40] have found the same anion in potassium tetraborate tetrahydrate. The rings contain two triangular and two tetrahedral borate groups joined at common oxygen atoms. The two tetrahedral groups are further linked by means of an oxygen bridge across the ring. All off-ring oxygen atoms are hydrated in borax.

As noted in the previous study the alkali borates yield very poorly resolved spectra under the conditions used here. From the tabulated absorption bands it is noted that all the materials show similar spectra and probably all contain the basic $[B_4O_5(OH)_4]^{-2}$ anion

Table 8. *Infrared absorption spectra of* $Me_2O \cdot 2B_2O_3 \cdot XH_2O$ *compounds*

Kernite	Tincalconite	Borax	$K_2O \cdot 2B_2O_3 \cdot 4H_2O$ synthetic
	3500 sb	3500–	
	3340 vsb	3000 vsvb	
	3000 svb		
	2400 svb	2000 svb	
1700 mvb	1630 mvb	1620 mvb	1625 mvb
1460 m	1455 msh	1450 msh	
1425 msh	1405 svb	1390 svb	1395 svb
1340 vsvb	1340 vsvb	1330 vsvb	1320 vsvb
	1190 msh	1275 mvb	
1160 m	1155 sb	1155 mb	1220 s
	1125 svb	1123 mvb	1160 m
1075 mb	1075 svb	1070 mb	1080 sb
1010 svb	1025 svb		1060 msb
	985 sb	980 sb	970 sb
950 vsvb	940 sb	955 sb	905 sb
865 svb			
820 svb	805 sb	800 svb	805 svb
	750 mvb	750 svb	745 w
			710 m
685 mvb	665 mvb	665 mvb	665 mb
			600
	600 mvb	595 wb	560 mvb
550 s	520 mvb	505 mshvb	490 m
495 mb	425 mvb	420 sb	460 mb
455 mb		395 s	422 mvb
425 mvb			390 m

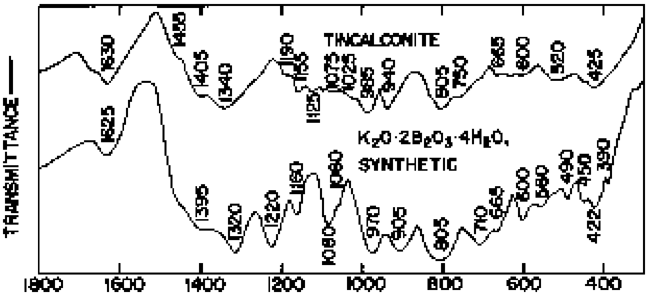


Figure 7. *Infrared absorption spectra of* $Me_2O \cdot 2B_2O_3 \cdot XH_2O$ *compounds.*

in some state of hydration or polymerization. The specimen of $K_2B_4O_7 \cdot 4H_2O$ used was obtained from a commercially available reagent labeled $K_2B_4O_7 \cdot 5H_2O$. The x-ray diffraction pattern of this compound can be indexed readily from the unit cell data of Marezio et al., [40] and it has been tabulated as the tetrahydrate.

The previous data obtained on this group of materials together with the present data exhibit a confusing pattern. The spectra for borax of Miller and Wilkins [4] and of Moenke [7] agree with each other but differ considerably from that of Akhamanova [14] and the present results. Miller and Wilkins [4] reported the spectrum of $K_2B_4O_7 \cdot 5H_2O$ which closely resembles their spectrum of borax but differs considerably from the spectrum of $K_2B_4O_7 \cdot 4H_2O$ obtained here. Takeuchi's [5] results for kernite agree well with the present data but both disagree in many respects with the results of Moenke [7]. The overall lack of agreement between the spectra obtained by different workers appears to be greatest for these materials. This question will be discussed later.

6.2. The $Me_2O \cdot 5B_2O_3 \cdot XH_2O$ Compounds

Data for the minerals ammonium larderellite and ammonioborite [41] and the synthetic 1:5:10 sodium borate are given in table 9. Representative spectra are not shown because there is strong absorption and poor resolution throughout the entire spectral range. The strong absorption is to be expected in the two ammonium compounds because they contain the infrared active NH_4^+ ion in addition to water of hydration and a complex borate anion. Christ [16] has predicted that sborgite, larderellite, and ammonioborite have the same anion and the data of table 9 confirm this prediction for the ammonium compounds with little question. The spectrum of the 1:5:10 synthetic sodium borate differs from those of the ammonium borates in many details but not in gross features. Because of the unknown effect of the NH_4^+ ion on the spectra, it is possible that all three compounds contains similar anions.

TABLE 9. *Infrared absorption spectra of* $Me_2O \cdot 5B_2O_3 \cdot XH_2O$ *compounds*

$Na_2O \cdot 5B_2O_3 : 10H_2O$ synthetic	Ammonioborite	Larderellite
1670 mb	1650 mvb	
	1425 vsvb	1425 vsvb
1375 vsvb	1350 vsvb	1350 vsvb
1300 vsvb	1235 vsvb	1225 mvb
1195 m	1190 sb	1185 s
1145 svb	1160 mb	1165 m
1075 sb	1085 sb	1085 mvb
1045 m	1055 sb	1055 mb
1010 sb	1015 svb	1015 mvb
950 m	940 svb	940 mb
925 s	915 sb	920 mvb
910 s	880 w	880 w
780 s	820 mvb	810 mb
765 s	775 sb	775 s
675 vsvb	740 m	
470 mb	675 sb	675 mvb
440 mb	545 s	545 s
375 mvb	510 mb	455 m
	460 mb	425 mvb

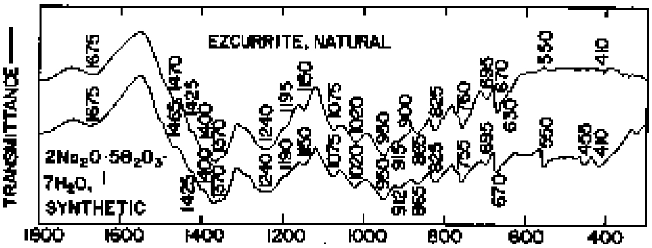


FIGURE 8. *Infrared absorption spectra of* $2Na_2O \cdot 5B_2O_3 \cdot 7H_2O$ *compounds.*

6.3. The $2Me_2O \cdot 5B_2O_3 \cdot XH_2O$ Compounds

Ezcurrite and the $2:5:X$ synthetic sodium borates show rather poor spectra characterized by strong absorption throughout the spectral range studied. The absorption bands observed are listed in table 10 and figure 8 shows the spectra for a synthetic and a natural ezcurrite. It is obvious from figure 8 that despite the rather poor resolution that these materials are almost certainly the same insofar as the anions are concerned. In addition, the fact that, band for band the frequencies are the same within experimental error may be interpreted to mean that the materials are chemically and structurally identical. This conclusion is based on previous studies which showed that change of anion or crystal structure generally produces shifting of some bands in the infrared spectrum [42]. The close similarity in the spectra of all three minerals listed in table 10 indicates that the anions are similar.

TABLE 10. *Infrared absorption spectra of* $2Me_2O$ $5B_2O_3$ XH_2O *compounds*

Ezcurrite	$2Na_2O \cdot 5B_2O_3 \cdot 5H_2O$ Synthetic	$2Na_2O \cdot 5B_2O_3 \cdot 4H_2O$ Synthetic
1675 mvb	1625 mvb	1650 mvb
1470 mb	1465 mb	1440 mvb
1425 m		
1400 mbsh	1400 mb	1360 svb
1370 vsb	1350 vsvb	1325 svb
1240 sb	1245 svb	1250 mvb
1195 msh		1230 svb
1150 m		1150 m
1075 mb	1045 mvb	1070 sb
1020 mb	1015 svb	1030 svb
950 sb	945 svb	925 sb
915 m		
900 w		
865 m	870 m	880 svb
825 m	825 mvb	830 mvb
760 m	740 mvb	740 mvb
695 m	695 mb	695 mvb
670 s	670 mvb	650 mb
	630 w	600 mvb
550 w	550 mvb	550 m
455 w	455 mvb	440 mb
410 mb	410 mvb	

6.4. Miscellaneous Borates

Data for three borates not readily classified with the previous groups are given in table 11 and the spectra are shown in figure 9. The data for szaibelyite and

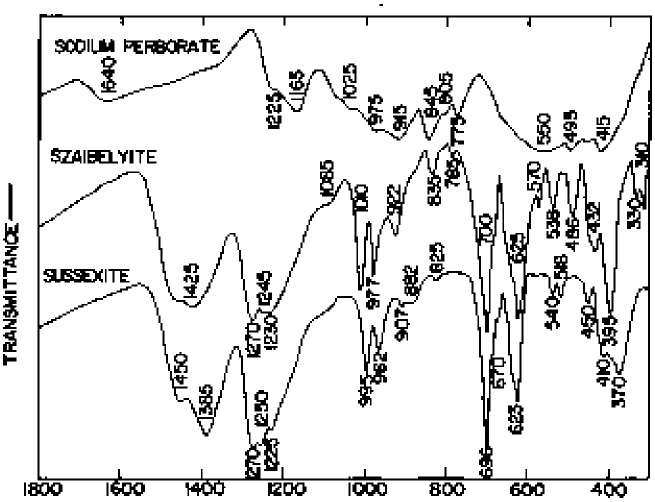


FIGURE 9. *Infrared absorption spectra of miscellaneous hydrated borates.*

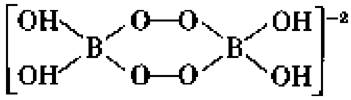
TABLE 11. *Infrared absorption spectra of miscellaneous borate compounds*

$NaBO_3 \cdot 4H_2O$ sodium perborate	Szaibelyite	Sussexite
3590 s	3555 s sharp	
3500–3000 svb	1425 vs	1450 sb
1640 wvb	1270 s	1365 s
1225 msh	1245 s	1270 s
1165 mvb	1230 s	1250 s
1025 mb	1085 msh	1225 m
975 sb	1010 s	995 m
915 svb	977 s	962 m
845 sb	922 m	907 m
805 m	835 m	882 mb
775 mb		825 w
550 svsb	785 w	696 s
495 sh	700 vs	670 msb
415 sb	625 s	625 s
	570 m	540 m
	538 m	518 m
	486 m	450 m
	432 m	410 m
	395 s	370 sb
	330 m	
	310 m	

sussexite agree reasonably well with the results obtained by Takeuchi [5] for camsellite (szaibelyite) and sussexite and with the results of Plyusnina and Kharitonov [15] for ascharite (szaibelyite). From his spectra, Takeuchi [5] concluded that the anion in these compounds was the pyroborate ion while Plyusnina and Kharitonov, apparently being unaware of Takeuchi's earlier work, noted that the spectrum of ascharite was similar to that of $LaBO_3$ which contains a triangular borate anion. However, the latter workers concluded tentatively that the complexity of the spectrum indicated a more complex ion than the simple triangular ion [15]. Akhamanova independently arrived at the same conclusion [14].

The structure of this anion has been reported to be a singly hydrated pyroborate group, with some uncertainty as to the exact structure [43] caused by translation. It is not clear that both borons are coordinated with three oxygen atoms. However, the spectrum clearly indicates that there is no tetrahedral boron present in the structure. From the earlier work on the pyroborates [1] it appears that the spectrum of anhydrous magnesium pyroborate becomes considerably less complex in the ν_2 region on hydration but more complicated in the ν_1 region. Tentative assignments are possible for many of the bands in the spectrum of szaibelyite on the basis of the spectrum of anhydrous magnesium pyroborate and the known spectrum of triangular borate groups. These are obvious and need not be specified here.

In sodium perborate the anion has been reported [44] to consist of two partly hydrated tetrahedral borate groups connected through peroxide linkages and to have the structure



$$\left[\begin{array}{c}OH\\OH\end{array}B\begin{array}{c}O-O\\O-O\end{array}B\begin{array}{c}OH\\OH\end{array}\right]^{-2}$$

The structural formula of sodium perborate may be written $Na_2[BO_2(OH)_2]_2 \cdot 6H_2O$. This anion is unlike any previously encountered here and its spectrum is likewise unique as shown in figure 9. In this spectrum the 3590 cm^{-1} band indicates some nonhydrogen bonded OH and the broad strong band between 3500 and 3000 cm^{-1} shows that much of the OH is hydrogen bonded. The weak 1640 cm^{-1} band is attributed to the bending mode of H–O–H, and the medium broad bands at 1225 and 1165 cm^{-1} to the B–OH bending modes plus overtones and combinations. The strong absorptions at 915 and 845 cm^{-1} are derived from the ν_3 tetrahedral modes and the doublet is indicative of tetrahedral coupling as noted earlier. The strong broad band at low frequencies probably contains modes derived from ν_2 and ν_4 of tetrahedral units plus OH torsional modes. The complexity of the band indicates the presence of several overlapping bands. The spectrum for this material has been reported by Miller and Wilkins [4] with reasonably good agreement between the data.

7. Reliability of Infrared Spectra of Hydrated Borates

In comparing the spectra of different workers it has been noted that the agreement was not satisfactory. It is to be expected that on a given material, the same infrared bands having similar relative intensities should be obtained. Some latitude in the exact frequencies reported (i.e., a few cm^{-1}) and perhaps in the detection of weak bands might be expected. For the hydrated borates it is clear that data do not agree to this extent and it is desirable to examine possible reasons for the discrepancies.

The discordance in the data must be traced to one or more of three sources; first, the materials themselves; second, the preparation techniques used to prepare the materials for study; and third, the actual measurements. Of these three sources the third can probably be dismissed as a real source of error. There is no evidence that any appreciable errors in band positions exist between the results obtained on different spectrometers. In fact the evidence is that the spectrometers agree within experimental error because many strong bands can be identified in spectra of various workers which agree within the frequency limits expected. It is believed, therefore, that the real causes for the discrepancies are to be attributed to variation in the materials or differences arising from techniques of preparation.

Insofar as the identity of the materials investigated is concerned, the previous reports give little information. Miller and Wilkins used chemical reagents in their studies [4]. Takeuchi [5] reports that his substances were carefully selected and were well-developed crystals of highest purity. Plyusnina and Kharitonov [15] used single crystals, but Akhamanova [14] and Moenke [7] give no details of the method used for selection of their specimens. In the present study most of the materials were of the highest purity presently available as judged by microscopic examination and x-ray powder diffraction. It must be noted, however, that neither these methods nor that of selecting natural single crystals ensures that the specimens are free of contaminants. If the contaminants should consist of other borates (all of which are strongly active in the infrared) even in small quantity, it is clear that some differences in the spectra may result. In addition to the question of purity, there remains a problem associated with the degree of crystallinity of the specimen. Most of the borates yield complex spectra containing many broad, obviously complex bands, containing unresolved structural details. Experience in this laboratory has indicated that two specimens of identical composition but differing either in degree of crystallinity or perhaps in perfection of crystallites can yield spectra which are very similar in gross appearance but remarkably different in detail. Broad featureless bands frequently show many resolvable details when the degree of crystallinity of the specimen is apparently improved. It appears most probable that discrepancies in the spectra of various workers consisting of differences in numbers of bands reported is to be attributed either to actual contamination of the specimens by other borates (or other spectrally active chemical species) or to differences in the crystallinity of the specimens.

Insofar as the specimen preparation techniques are concerned, the problem of purity is also involved but in a different manner. Here the concern is with the actual identity of the materials studied because of changes in degree of hydration or of interaction with the alkali halide windows used. The various workers used the following techniques of sample study: Miller and Wilkins and Takeuchi—mulls with hydrocarbon or fluorocarbon liquids using salt (NaCl?) plates [4, 5]; Moenke—pressed pellet technique using vacuum formation of KBr pellets [7]; Akhamanova—film deposited on KBr plates by evaporation of isobutyl alcohol dispersing medium [14]; Plyusnina and Kharitonov—films deposited on KCl or NaCl plates by evaporation of isopropyl alcohol [15]; present work—films deposited on CsBr plates by evaporation of CCl_4. It is well known that solids (and in particular hydrates) interact with the alkali halides and that the interaction produces changes in the spectra. Of the methods used, it would appear that the mull technique is the most preferable from the viewpoint of lessening such interactions, the film method next, and the KBr pellet the most objectionable. In addition to the increased probability of interaction in KBr pellets must be added the undesirable procedure of subjecting the hydrated borates to vacuum in the pellet forming process. Reduction in pressure might affect the state of hydration of the small quantity of hydrate present. It seems very probable that differences in positions of bands observed by different workers may be caused by shifts due to interaction with the alkali halide windows used.

In addition to the question of interaction with the alkali halide there is some uncertainty introduced by the mechanical and thermal effects of the fine grinding required to produce particles sufficiently small for infrared study. As noted earlier, the spectra for borax, a chemically pure reagent, obtained by different workers differ radically. C. J. Bowser [45] has obtained evidence showing that in KBr pellets, borax produces the spectrum of tincalconite, a lower hydrate. Thus the spectra for borax of Miller and Wilkins [4] and Moenke [7] which agree very well actually appear to represent tincalconite. Dehydration of borax can be understood in the KBr pelleting process but is hard to visualize in the mull technique, unless it occurs during grinding. Therefore, it is necessary to include the fine grinding technique among the details which might produce differences in the spectra.

It is concluded that the infrared spectra of the hydrated borates, at present, are not of acceptable reliability. The lack of reproducibility is most probably to be attributed to differences in chemical composition and degree of crystallinity and to varying interactions between the hydrated borates and the alkali halide windows. Production of definitive spectra will require systematic study of the effect of these disturbances.

8. Identification of Borate Minerals by Infrared Spectroscopy

H. Moenke has studied the infrared spectra of several hydrated borate minerals in a series of papers generally oriented toward differentiating among various borates [6–13]. As a result of his study he concluded that the spectral method could be used to identify hydrated borate minerals and has pointed out identifying features in the spectra of various minerals.

It is clear from the immediately preceding discussion and the comparisons between spectra made throughout this report that the present conclusions must disagree with the idea of identification by infrared methods. The fact that there is a disturbing amount of disagreement between the spectra of various workers at the present time would appear to invalidate the use of spectroscopy as a method of identification. Moreover, the spectra of most borates are so complex that it seems imperative to obtain at least a degree of understanding of the origin of the spectral bands before identification of minerals of this type is attempted on the basis of their spectra. In the case of the simpler spectra, i.e., sussexite, hambergite, etc., identification by means of infrared spectroscopy is believed to be possible. However, if such minerals were contaminated with other borates (as for example sussexite contaminated with szaibelyite) identification would be almost impossible.

9. Conclusions

The infrared spectra of the hydrated borates are considerably more complex than the spectra of the anhydrous analogues. The increased complexity arises from the effects of the hydration of the borate anions and hydrogen bonding between anions. The effect of the hydrogen bonding appears to produce noticeable changes in most of the borate anion fundamentals and results in complicating the spectrum throughout the frequency range 400–4000 cm^{-1} studied here. Thus the effects are by no means restricted to the region commonly considered to be diagnostic for OH.

As a result of the increased number of bands the spectra are frequently poorly resolved and detailed interpretation appears to be remote. It is unlikely that any hydrated borate anion can be identified solely from its infrared spectrum. However, the previous conclusions concerning identification of three-fold and four-fold coordinated boron appear to be equally valid in the hydrated and anhydrous borates. For the hydrated compounds the conclusions are more uncertain because strong bands near 1200 cm^{-1} apparently arising from B – OH bending modes fall into the region previously considered as indicative of trigonal borate groups. Any serious attempt to understand the spectra of the hydrated borates will probably require deuteration as well as boron isotope substitution.

At the present time agreement between spectra obtained by different investigators is not considered to be satisfactory. The probable causes of the disagreement are believed to originate in differences in the materials themselves or from varying degrees of interaction with the alkali halide cells used. As a result of the lack of agreement between various workers as well as the inherent complexity of the spectra it is considered that borate minerals cannot be identified at this time on the basis of their infrared spectra alone.

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