Infrared spectrum of synthetic isotopic species of sinhalite, MgAlBO₄

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Abstract—The i.r. spectra of isotopic species of synthetic sinhalite, $MgAlBO_4$, are reported and discussed in relation with a group theoretical analysis. The stretching vibrations of the BO_4 group are observed in the 1150–800 cm^{-1} region, but no significant ^{10}B–^{11}B isotopic shift is observed in the lower wavenumber region: the identification of the BO_4 bending vibrations is thus impossible; these vibrations are very probably mixed up with lattice vibrations. Several translational modes of the Mg cations have been identified in the 500–300 cm^{-1} region with the help of ^{24}Mg–^{26}Mg isotopic shifts. The possible assignments for Al translations are also discussed. The large splitting of the v_3 components of the BO_4 tetrahedron is discussed in connection with the vibrational behavior and the structure of other olivine-type compounds.

INTRODUCTION

Sinhalite, $MgAlBO_4$, is one of the very few anhydrous *ortho*-borates whose structure contains "isolated" BO_4 tetrahedra. The i.r. spectrum of the mineral has already been reported [1–3] but, in view of the complexity of the spectrum, the proposed interpretations are either restricted to a few bands [1] or doubtful [2, 3].

The assignment problem may be handled through the investigation of isotopic species [4] and, since sinhalite may be synthesized hydrothermally under moderate temperature and pressure conditions [5], it was decided to synthesize the possible isotopic species of sinhalite, and to investigate their vibrational spectrum.

EXPERIMENTAL

Synthesis of the compounds

All syntheses were carried out in Bochum by the hydrothermal treatment of gels of suitable composition [5]. The following conditions were chosen: $T = 700°C$; $p = 3$ kilobars; duration about 500 h; 50% boron (H_3BO_3) in excess.

The purity of the resulting samples was checked by X-ray diffraction. Most of the samples were quite pure, but some contained a small quantity of $Mg_2B_2O_5$ or $MgAl_2O_4$; this quantity proved too small to cause significant modifications of the i.r. spectrum.

Isotopic compounds. Boron (H_3BO_3) was available either as natural B (essentially ^{11}B) or enriched in ^{10}B. Likewise, MgO was used either with the natural isotopic composition (essentially ^{24}Mg) or enriched in ^{26}Mg. By contrast, Al is a monoisotopic element (100% ^{27}Al), and isotopic replacement is not possible. The isotopic purity data are collected in Table 1.

Spectra

The i.r. spectra were registered by the conventional pressed disc technique with a Beckman 4250 spectrophotometer (2000–300 cm^{-1} region). We also tried to investigate the Raman spectrum (Ar⁺ laser; Coderg PHO double monochromator), but the results were of poor quality (a very weak spectrum merged into a strong continuous background), and they will not be discussed here.

Table 1. Isotopic purity data

Element		Isotopic composition (in mole %)
Mg (natural)	^{24}Mg	78.60
	^{25}Mg	10.11
	^{26}Mg	11.29
^{26}Mg*	^{26}Mg	99.70
B (natural)	^{10}B	18.83
	^{11}B	81.17
^{10}B*	^{10}B	92.41
	^{11}B	7.59

*Purchased from Oak Ridge National Laboratory.

CRYSTAL STRUCTURE AND VIBRATIONAL ANALYSIS

Sinhalite is orthorhombic, space group *Pnma*, isomorphous with olivine [6]. Boron occupies distorted tetrahedra (site symmetry C_s); aluminium and magnesium are located in octahedral sites, the first in the inversion symmetry site (site symmetry C_i), and the second on mirror plane positions (site symmetry C_s). A full group theoretical analysis for the olivine structure has already been reported [7] (in this paper, the space group was erroneously labeled *Pbnm*: the correct labeling is *Pnma*) and will not be repeated here. We shall just give the results of this analysis for the i.r.-active vibrations (Table 2). This analysis relies on the hypothesis that the separation of the vibrations into internal (BO_4 groups) and external modes is a satisfactory approximation. The validity of this assumption will be discussed later on.

Two interesting points are evidenced by this treatment:

i . The number of i.r. active fundamentals is rather large (35), and the corresponding spectrum is expected to be fairly complicated.

ii. Some internal modes which, for the isolated ion (point group T_d) belong to different representations

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Table 2. Symmetry properties of the i.r. active vibrational modes of sinhalite

Atom	Site symmetry	Normal modes
B	C_s	$\Gamma_B = \Gamma_{Mg} = 2B_{1u} + 1B_{2u} + 2B_{3u}$
Mg	C_s	
Al	C_i	$\Gamma_{Al} = 3B_{1u} + 3B_{2u} + 3B_{3u}$
		Librations
BO$_4$	C_s	$\Gamma_{libr} = 1B_{1u} + 2B_{2u} + 1B_{3u}$
		Internal modes
BO$_4$	C_s	$\Gamma_{v_1} = B_{1u} + B_{3u}$
		$\Gamma_{v_2} = B_{1u} + B_{2u} + B_{3u}$
		$\Gamma_{v_3} = \Gamma_{v_4} = 2B_{1u} + B_{2u} + 2B_{3u}$

Total (after subtracting the three acoustical modes, namely $1B_{1u} + 1B_{2u} + 1B_{3u}$): $\Gamma_{Tot} = 13B_{1u} + 9B_{2u} + 13B_{3u}$.

(e.g. v_1 and v_3), are now split into components, some of which belong to the same representation and are thus able to interact. For the same reason, the possibility of vibrational interactions between internal, librational and translational modes cannot be neglected. This possibility will be discussed under the heading Assignments.

RESULTS AND ASSIGNMENTS

A typical spectrum (MgAlBO$_4$ synthesized with the natural isotopic abundances of Mg and B) is represented in Fig. 1; the wavenumber values of the isotopic species are collected in Table 3.
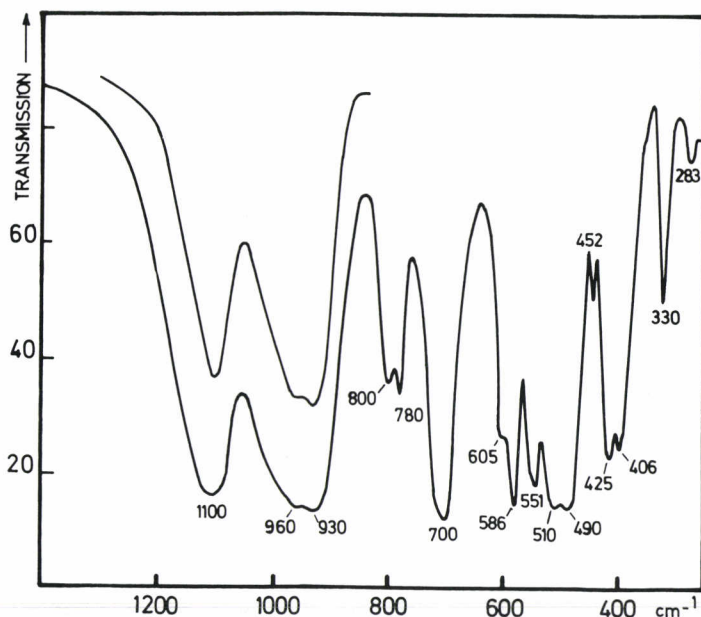
Fig. 1. Infrared spectrum of synthetic sinhalite MgAlBO$_4$ with natural isotopic abundances.

Table 3. Observed i.r. wavenumbers (cm^{-1}) of synthetic sinhalites

Natural isotopic abundances (three samples)			^{10}B	^{26}Mg (two samples)	
~1104	~1110	~1095	1138	~1113	~1107
960	960			~962	
930	933	930	995	927	927
800	800	800	803	~799	799
780	780	780	782	780	780
699	702	699	702	699	699
~605	~605	~605	~605	~603	~602
589	586	585	587	585	585
557	551	551	552	552	553
516	~510	(~506)	510	520	515
490	490	490	490	485	484
454	452	451	450	450	450
426	425	423	425	422	422
407	406	410	406	398	398
333	330	330	330	327	327
286	283	283	283	283	283
262	259	259	259	259	

Preliminary remarks

Before discussing the assignment problem, some comments must be made about the reproducibility of the wavenumber measurements. Some bands are fairly broad, particularly in the 1200–900 cm^{-1} region, and their position cannot be measured with accuracy. This lack of accuracy is the result, not only of the broadness of the band itself, but also of the fact that, for such broad bands, the position of the apparent absorption maximum depends on the granulometry of the sample. Although the greatest care was exercised during the grinding of the sample and the preparation of the KBr discs, the possibility of such spurious effects cannot be completely neglected. For this reason, we give (whenever possible) the wavenumber values measured in different samples, to get an idea about the reproducibility of the wavenumber values. This reproducibility is fair to good, depending on the broadness of the band, and this must be taken into account when considering the significance of the isotopic shifts.

Assignments

1150–900 cm^{-1} *region*. The broad bands in this region exhibit a very significant ^{10}B–^{11}B isotopic shift and are thus assigned to components of the v_3 antisymmetric stretch of the BO_4 tetrahedron. Three bands (in some spectra, two bands and a broad shoulder) are observed, against a total of five predicted fundamentals issued from v_3. This is not unexpected since, owing to the broadness of the bands, weak components may be completely hidden by the strong ones.

It is worthwhile to compare the observed isotopic shifts (about 25–30 cm^{-1}) with the calculated ones. A rigorous calculation is impossible, because the values of the v_4 bending wavenumbers are unknown (see below). However, a rough evaluation is possible by using the approximate formula [8]:

$$v_3^2/v_3^{*2} \approx \frac{1 + 4m_O/3m_B}{1 + 4m_O/3m_{*B}}$$

$$v_3/v_3^* \simeq 1.024$$

where v and v^* refers to the wavenumbers of the light and heavy isotopic species, respectively. m_O is the mass of the oxygen atom; m_B and m_{*B} are the masses of the light had heavy boron isotopes, respectively. Average values of 10.08 (for m_B) and 10.82 (for m_{*B}) were used to take into account the actual isotopic compositions.

The observed wavenumbers lead to the following values of the isotopic ratios:
for the highest wavenumber band (1110 cm^{-1})

$$v/v^* = 1.025;$$

for the lower wavenumber band (930 cm^{-1})

$$v/v^* = 1.027.$$

These values are slightly higher than the calculated one, but this latter is the result of an approximation.
800 cm^{-1} *region*. The two bands of this region are sharp, with a good reproducibility of the wavenumber measurements (Table 3). Thus, the small ^{10}B–^{11}B wavenumber shifts are possibly significant. As far as the i.r. active modes are concerned, the factor group analysis predicts the splitting of the symmetric stretch v_1 into two modes ($B_{1u} + B_{3u}$), and this is the most probable assignment for these two bands. If the small ^{10}B–^{11}B wavenumber shift is considered as significant, it is easily explained by the fact that some components of v_3 also belong to the B_{1u} and B_{3u} species, and thus are able to interact with the components of v_1. Such a mixing of v_1 and v_3 modes has already been shown in the Raman spectrum of synthetic forsterite Mg_2SiO_4 [7].

700–250 cm^{-1} *region*. In the sinhalite structure, the v_4 bending vibration of the BO_4 tetrahedron is split into five distinct modes (Table 2) which, according to their antisymmetric character, should be sensitive to the mass of the central atom. However, no significant ^{10}B–^{11}B isotopic shift is observed in the whole 700–250 cm^{-1} region.

To understand this apparent contradiction, the following points must be considered:

i. Besides the BO_4 bending vibrations, this spectral range is expected to contain most of the external modes: Mg, Al and BO_4 translations, and BO_4 librations. Some of these vibrations (e.g. Mg and Al translations) are expected to give strong bands which may completely overlap the weaker BO_4 bending vibrations.

ii. By application of the Teller–Redlich product rule to the internal v_3 and v_4 modes of a BO_4 group with ideal T_d symmetry, we obtain:

$$\frac{v_3 v_4}{v_3^* v_4^*} = \left(\frac{m_{*B}}{m_B} \cdot \frac{m_B + 64}{m_{*B} + 64} \right)^{1/2} = 1.031.$$

Taking for v_3/v_3^* the average experimental value of 1.026, we obtain $v_4/v_4^* = 1.005$.

This would give a wavenumber shift of 3 cm^{-1} only in the 700–600 cm^{-1} region, and 2 cm^{-1} near 450 cm^{-1}. These values are of course approximate ones (because of the experimental errors in the v_3 values, and the distortion of the BO_4 tetrahedron); but they should not be grossly in error and they show that, even without interactions with other vibrational lattice modes, the isotopic shifts related to the BO_4 antisymmetric bending modes must be small (and in fact nearly within the limits of experimental errors).

iii. When applying the Teller–Redlich rule, we have assumed a lack of interaction between internal and external modes. But in fact, all i.r. active vibrations belong to three representations only. Since the BO_4 bending vibrations and many external modes are present in the same spectral region, there are numerous possibilities of vibrational interactions, implying an additional reduction of the ^{10}B–^{11}B isotopic shifts.

Mg *translations*. Two bands only (490 and 406 cm^{-1}) exhibit ^{24}Mg–^{26}Mg isotopic shifts which are certainly significant. For two other bands (425 and 330

cm^{-1}), the shift is too small to be unequivocally assigned to a Mg mass effect. In forsterite, Mg_2SiO_4, the Mg translations have been identified in the same spectral region (500–250 cm^{-1}) [7], but the number of bands exhibiting a significant ^{24}Mg–^{26}Mg isotopic shift is much greater (seven bands). This is of course related to the greater number of Mg cations in the chemical formula.

Al *translations*. Because of the lack of isotopic data, and the possibility of vibrational interactions, no firm assignment can be proposed.

Nevertheless, it may be pointed out that, for MgO_6 octahedra, Mg translations are generally observed near and below 500 cm^{-1} [7–9]. It may be inferred that, for the same octahedral coordination and because of its higher valency, Al–O vibrations should give absorption bands at significantly higher wavenumbers. Indeed, figures of about 650 cm^{-1} have been quoted previously [8, 9].

For these reasons, the strong band at 700 cm^{-1} is assigned to an Al–O vibration. As other possible assignments for this band, we can consider:

—the symmetric BO_4 stretch (v_1); but the two predicted i.r. active modes have been observed at 800 and 780 cm^{-1}.

—one of the antisymmetric BO_4 bending modes. Although not completely impossible, this assignment is improbable in view of the wavenumber values proposed for this motion, namely 580 or 520 cm^{-1} (this point is discussed later). Other modes such as BO_4 symmetric bend, or BO_4 librations are expected to lie at still lower wavenumbers.

The identification of the remaining Al translations remains hypothetical.

<div style="text-align:center">DISCUSSION</div>

Vibrational wavenumbers of the BO_4 tetrahedron

We have collected in Table 4 the proposed wavenumber values for the BO_4 fundamental modes.

Some of these values have been calculated by comparison of the fundamentals of the similar groups, $(BO_3)^{3-}$, BF_3 and $(BF_4)^-$. The experimental values are those deduced from the experimental study of sinhalite.

It may be pointed out that the rather high figure of 700 cm^{-1} calculated by Ross for v_4 was later discarded by the same author and replaced by 580 cm^{-1} after an experimental study of sinhalite and $TaBO_4$ [2]. This assignment is deduced, not from isotopic data, but from the fact that both $MgAlBO_4$ and $TaBO_4$ exhibit an absorption band in this spectral region. This is a weak argument since, because of their different structures and chemical compositions, $MgAlBO_4$ and $TaBO_4$ exhibit rather different i.r. spectra, and the coincidence is probably fortuitous.

In an attempt to settle this point, we synthesized additional compounds whose structure contains "isolated" BO_4 tetrahedra, namely Fe_3BO_6 [12], $TaBO_4$ [13, 14] and Ni_2NbBO_6 [15], and we have investigated the i.r. spectra of their ^{10}B and ^{11}B isotopic species. The results are qualitatively similar to those given by sinhalite: the strong bands of the 1100–850 cm^{-1} region exhibit ^{10}B–^{11}B isotopic shifts of about 25 cm^{-1}. But much smaller (3 cm^{-1} or less), generally non-significant shifts, are observed in the 700–200 cm^{-1} region, in agreement with the low values deduced from the application of the Teller–Redlich product rule.

It must be added that *all* known structures characterized by the presence of isolated BO_4 tetrahedra also contain high-valency cations (Al, Fe, Nb, Ta) whose translational motions lie in the same spectral region than that of the BO_4 bending motions. The resulting overlapping and/or mixing of vibrations is a further difficulty in interpreting this region of the spectrum, and there seems to be little hope of solving unequivocally the problem of the bending vibrations of the tetrahedral $(BO_4)^{5-}$ anion.

The v_3 vibrations in olivine-like compounds

A striking feature of the sinhalite i.r. spectrum is the large splitting (about 180 cm^{-1}) of the components derived from v_3; it is tempting to correlate this splitting with the strong distortion of the BO_4 tetrahedron, the B–O distances going from 1.458 to 1.580 A [6].

In fact, a large splitting of the v_3 components is not restricted to sinhalite, and seems to be a general rule in the i.r. spectra of olivine-type compounds. However, Table 5 shows that this is not necessarily related to large differences in the cation–oxygen distances within

Table 4. Calculated and observed fundamental wavenumbers (cm^{-1}) of the $(BO_4)^{5-}$ anion

Tetrahedral group	v_3	v_1	v_4	v_2	Reference
$(BF_4)^-$	1075	769	524	353	Obsd. [10]
$(BO_4)^{5-}$	1030	750	520	380	Calc. [10]
	1050	854	702	481	Calc. [11]
	1085	864*	580	400	Obsd. [2]
	+ 920			376*	
	1100	800	?	?	Obsd. This work
	+ 930	+780			

*Raman spectrum.

Table 5. Splitting of the v_3 variation and cation–oxygen distances in the tetrahedral group of olivine-type compounds

Compound	v_3 splitting and reference	X–O tetrahedral distances and reference		
Sinhalite MgAlBO$_4$	180 cm^{-1} (this work)	B–O$_1$ B–O$_2$ B–O$_3$	1.458 Å [16] 1.580 1.459	($\times 2$)
Olivine	110 cm^{-1} [16]	Si–O$_1$ Si–O$_2$ Si–O$_3$	1.613 [17] 1.654 1.637	($\times 2$)
LiMnPO$_4$	160 cm^{-1} [18]	P–O$_1$ P–O$_2$ P–O$_3$	1.545 [19] 1.526 1.547	($\times 2$)
Mg$_2$ (Si$_{0.01}$ Ge$_{0.99}$) O$_4$ solid solution	98 cm^{-1} [16]			
LiMn (P$_{0.02}$ As$_{0.98}$) O$_4$ solid solution	98 cm^{-1} [18]			

the tetrahedral group: the most evident case is that of LiMnPO$_4$, with a v_3 splitting of 160 cm^{-1} [18], whereas the P–O distances are not significantly different [19]. To explain this large splitting, two other factors must be considered, separately or simultaneously: a large factor group splitting, due to strong vibrational interactions between nearest neighbor tetrahedral groups; and/or an unequal distribution of the bonding forces within the XO$_4$ tetrahedron.

The factor group splitting may be suppressed by the study of appropriate dilute solid solutions such as Mg$_2$ (Si$_{0.01}$ Ge$_{0.99}$)O$_4$, where the SiO$_4$ groups are dispersed in a host lattice still having the olivine structure. In this case, the v_3 splitting of the SiO$_4$ is reduced to the site group splitting. The results quoted in Table 5 show that, for Mg$_2$SiO$_4$ and LiMnPO$_4$, this site group splitting is still rather large. Since, at least for the phosphate, the geometrical deformation is not important, this must be assigned to an unequal distribution of the bonding forces in the PO$_4$ tetrahedron.

This is qualitatively explained by the fact that, in the olivine structure, each oxygen atom of the XO$_4$ tetrahedra is also bound to three octahedral cations C$_{oct}$, whose environment is strongly distorted: the inequality in the C$_{oct}$–O bond induces a corresponding inequality in the X–O tetrahedral bonds.

SUMMARY

The i.r. spectrum of synthetic sinhalite MgAlBO$_4$ was investigated with the help of ^{10}B–^{11}B and ^{24}Mg–^{26}Mg isotopic replacements. This leads to the unambiguous identification of the BO$_4$ stretching vibrations and of some of the Mg^{2+} translations predicted by a group theoretical analysis. The large splitting of the v_3 vibrations is probably due, at least in part, to an unequal distribution of the bonding forces within the BO$_4$ tetrahedron.

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