

Vibrational spectrum of crystalline and glassy LiBGeO_4 : structural analogies with BAsO_4

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Lithium borogermanate, LiBGeO_4 , has been considered as a possible material for non-linear applications, because of the lack of a centre of symmetry. Another interesting possibility is the easy formation of a glass. The existing crystallographic data are, however, controversial: according to Ihara [1], the structure is orthorhombic pseudotetragonal, space group $Fmm2$, whereas a true tetragonal cell, probable space group $I\bar{4}$, is proposed in a more recent paper [2]. Twinning of the crystals prevented a full structure determination, but the authors of the latter paper proposed a structural analogy with cristobalite-like BPO_4 and BAsO_4 . We present here additional structural information deduced from a study of the vibrational (infrared and Raman) spectra, together with some other properties of this compound.

LiBGeO_4 has been synthesized by solid state reaction between stoichiometric quantities of Li_2CO_3 , H_3BO_3 and GeO_2 . The mixture is progressively heated in a covered platinum crucible up to a final temperature of 830°C , and this temperature is maintained for a total of 4 days with intervening mixing and grinding. Apart from small differences in the relative intensities of the diffraction peaks, the X-ray powder diagram (monochromatized $\text{CoK}\alpha$ radiation) is practically identical to that published by Liebertz and Staehr [2]. Glassy LiBGeO_4 was obtained by melting the pure compound at 1000°C for 10 min and air quenching. No weight loss was observed. Some difficulties were experienced in synthesizing pure BAsO_4 , probably because of the low thermal stability of this compound. The following procedure gives satisfactory results. Arsenic acid (as $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, Merck P.A.) is well ground and mixed with an excess of boric acid, so as to obtain a B:As molar ratio of 1.25. The mixture is very progressively heated to 150 to 200°C to expel water, and heating is then resumed up to 500°C for 4 to 5 days. The resulting white solid is then washed with absolute methanol (not water) to eliminate excess boric acid. The residue is pure BAsO_4 , as shown by X-ray diffractometry, but the high-angle diffraction peaks are not very sharp. Some improvement in crystallinity is observed after heating for 1 h at 720°C . The infrared spectra were registered with a Beckman 4250 spectrometer (2000 to 300cm^{-1} region; KBr discs) and a Polytec FIR 30 interferometer (350 to 30cm^{-1} region; polyethylene discs). The Raman spectra were obtained with an Ar^+ laser (100 to 200 mW; 514.5 nm green line). For the conductivity measurements, a small quantity (2 to 3%) of gum-arabic is added to the powdered LiBGeO_4 ; the mixture is pressed into a disc (diameter 18 mm, thickness 1.2 mm) which is then progressively heated

up to 800°C . The compactness is about 75%. Silver paint is applied to the faces, and a.c. conductivity is measured between 300 and 600 K at a 100 kHz frequency with a universal bridge.

Typical spectra of LiBGeO_4 and BAsO_4 are reproduced in Figs 1 and 2. The observed vibrational frequencies, including ^{10}B and ^6Li isotopic values, are collected in Table I. The following characteristic features are immediately evident from the spectra.

(i) No band is observed in the 1100 to 1300cm^{-1} region in the infrared spectrum of crystalline LiBGeO_4 ; moreover, the strong band observed at 947cm^{-1} is shifted to 969cm^{-1} when natural boron (predominantly ^{11}B) is replaced by ^{10}B . The coordination of boron is thus tetrahedral.

(ii) The existence of very sharp bands points to an ordered distribution of the BO_4 and GeO_4 tetrahedra.

(iii) The analogies with the spectrum of BAsO_4 are striking: nearly all bands of LiBGeO_4 have their counterpart in the spectrum of BAsO_4 . The only evident difference is the weak band near 300cm^{-1} in the Raman and infrared spectrum of LiBGeO_4 , which is clearly missing in the spectrum of BAsO_4 . But this band is shifted by about 16cm^{-1} towards higher frequencies when natural lithium (essentially ^7Li) is replaced by ^6Li (Table I): its assignment to a lithium translation is thus straightforward.

More detailed assignments will be considered below.

Finally, Table I shows the existence of clear-cut Raman-infrared coincidences: this is additional proof of the lack of a centre of symmetry. Moreover, all the coincidences observed in the spectrum of BAsO_4 have their counterpart in the spectrum of LiBGeO_4 . This shows that both compounds have the same symmetry properties, and reinforces the structural analogy already deduced from the overall similarity of the spectra.

The spectrum of the glass (Fig. 2) is characterized by:

(i) a strong additional absorption centred near 1400cm^{-1} , showing the formation of a lattice of BO_3 triangular units. This partial transformation of BO_4 into BO_3 groups associated with the glass formation is common to all compounds containing BO_4 tetrahedra in the crystalline state [3] and, to the best of our knowledge, no glass containing only BO_4 tetrahedra has been evidenced so far;

(ii) two poorly separated broad bands in the 1000 to 800cm^{-1} region, corresponding to the stretching motions of BO_4 and GeO_4 tetrahedra;

(iii) a nearly "flat" absorption between 600 and 200cm^{-1} . We have shown [4], and this has been confirmed in later papers [5] that the Li^+ cation in glasses

TABLE I Vibrational frequencies (cm^{-1})

LiBGeO ₄			BAsO ₄						
Raman			Infrared			Raman		Infrared	
⁶ Li ^a BGeO ₄	⁷ Li ^b B	¹⁰ Li ^c B	⁶ Li ^a B	⁷ Li ^b B	¹⁰ Li ^c B	⁷ BAsO ₄	¹⁰ BAsO ₄	⁷ BAsO ₄	¹⁰ BAsO ₄
239	240	240	243	243	243*	216	217	217	217*
248	249	247				220	220		
318	302	301	316	299	300*				
375	373	373				381	381		
413	412	411	417	410	410*	395	395	408	405
471	472	473	488	486	486			488	488
533	532	532				501	501		
600	600	600	600	600	602*	582	581	580	579*
757	757	761	757	757	761*	813	823	809	*
809	809	811	809	810	812*	857	867	857	866*
923	921	921	944	947	969	990	990	965	977
1100	1099	1118				1119	1136		

* Infrared-Raman coincidences.

gives an extremely broad absorption centred near 400 cm^{-1} . An additional contribution certainly comes from the bending vibrations of the $\text{BO}_4 + \text{GeO}_4$ lattice.

To confirm the structural analogy indicated by the vibrational spectra, we have recorded the X-ray powder diagrams of LiBGeO_4 and BAsO_4 under the same experimental conditions. The analogy is nearly perfect, even in the peak relative intensities (Fig. 3).

The DTA experiments were carried out at heating and cooling rates of 600°C h^{-1} . No thermal event was observed with crystalline LiBGeO_4 , apart from a strong endotherm peaking at 898°C (melting point 902°C , according to Liebertz and Staehr [2]). Glassy LiBGeO_4 gives a strong crystallization exotherm at 628°C , followed by the melting endotherm at 897°C . No thermal effect is observed during the cooling stage and the sample is recovered as a glass.

The a.c. conductivity is negligible between 300 and 600 K.

A more detailed interpretation of the spectrum may be obtained by considering the results of a factor group analysis. For BAsO_4 (space group $I\bar{4}$, $Z = 2$; Wyckoff positions: 2 P in 2a; 2 B in 2c; 8 O in 8g), we find, after subtracting the acoustical modes:

$$\Gamma_{\text{vibr}} = 3A + 4B + 4E$$

The fully symmetric A modes are only Raman active; the oxygen atoms only are allowed to move during these vibrations, whilst the B and As atoms are necessarily at rest.

One of these modes may be described as a stretching vibration of the oxygen atoms between motionless B and As cations. The restoring force is thus provided by the sum of the B-O and As-O bonds and should lead to a fairly high frequency: this is probably the strong, sharp Raman peak at 990 cm^{-1} (921 cm^{-1} in LiBGeO_4) with zero shift for the $^{10}\text{B}-^{11}\text{B}$ replacement. The two remaining A modes are bending vibrations. One is probably the strong Raman peak at 500 cm^{-1} (532 cm^{-1} in LiBGeO_4); the third cannot be identified with certainty.

The B and E modes are both Raman and infrared active, and allow the displacement of all atoms.

Four bands exhibiting significant $^{10}\text{B}-^{11}\text{B}$ isotopic shifts are observed in the high-frequency region and are assigned to stretching vibrations (Table I). Because we are dealing with a lattice of BO_4 and AsO_4 tetrahedra interconnected by common oxygen atoms, the existence of localized vibrations specifically related to either BO_4 or AsO_4 tetrahedra is very unlikely.

The moderate values of the observed $^{10}\text{B}-^{11}\text{B}$ isotopic shifts (10 to 17 cm^{-1}) point to the existence of

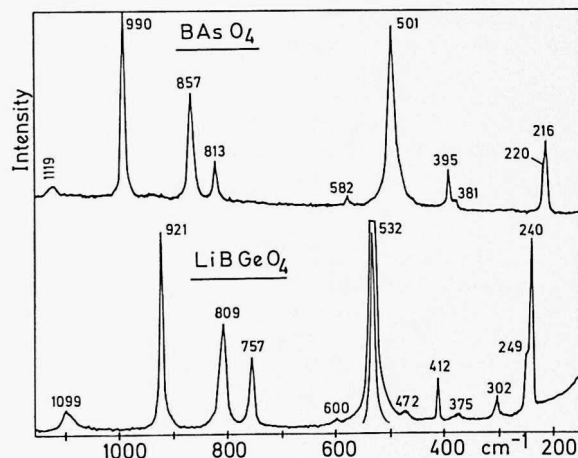


Figure 1 Raman spectra of BAsO_4 and LiBGeO_4 . No band is observed below 200 cm^{-1} .

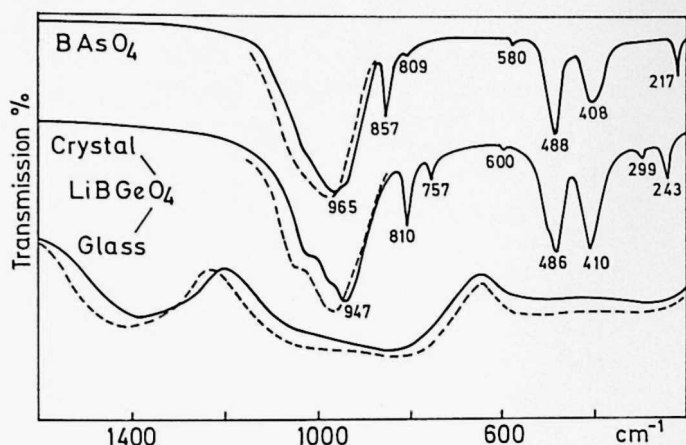


Figure 2 Infrared spectra of BAsO_4 and LiBGeO_4 , crystal and glass. (—) Boron with natural isotopic composition, (---) boron enriched in ^{10}B (92.4%). No band is observed below 200 cm^{-1} .

mixed $\text{BO}_4 + \text{AsO}_4$ vibrations. The lower frequency bands (below 600 cm^{-1}) correspond to bending motions, but it does not seem possible to propose more precise assignments. The assignment problem is further complicated by the fact that 13 distinct frequencies are observed in the combined Raman and infrared spectra, against a total of 11 predicted modes. Possible explanations are as follows.

(i) A few weak bands are due to impurities. This is unlikely, because different samples (obtained in different syntheses) give quite reproducible spectra.

(ii) The crystal symmetry is lower than $I\bar{4}$. This is again unlikely, because the structure seems to be firmly established [6].

(iii) The symmetry properties of the crystal allows the splitting of the B and E vibrations into LO and TO modes, which could appear as separate peaks in the Raman spectrum. Because the crystal is not very ionic, the LO components are expected to be very weak or missing in the Raman spectrum, but we can explain in this way the weak 220 cm^{-1} shoulder, which could be the LO component of the vibration giving the 217 cm^{-1} peak (TO mode). Likewise, the LO-TO splitting may be responsible for the broadening of some infrared bands. In this case, one vibrational mode may appear at significantly different frequencies in the infrared and Raman spectra and thus may be erroneously accounted for as two separate vibrational modes (e.g. the 408 to 395 cm^{-1} pair).

If we assume that BAsO_4 and LiBGeO_4 are isostructural, the preceding discussion and assignments can be extended to LiBGeO_4 . In this latter case, the five stretching modes are located at significantly lower frequencies; this is easily explained by the fact that the

$\text{Ge}^{\text{IV}}-\text{O}$ bond is weaker than the $\text{As}^{\text{V}}-\text{O}$ bond, whereas the contribution of the weak $\text{Li}^{\text{I}}-\text{O}$ bond is negligible.

Conversely, the bending frequencies are nearly the same, or higher for LiBGeO_4 than for BAsO_4 : the presence of lithium filling some voids of the cristobalite-like lattice (see discussion below) introduces an additional restoring force, even though the lithium itself does not move during the vibrations under consideration.

The localization of lithium cannot be deduced from the vibrational spectrum alone, because the study of various lithium compounds has shown that the Li-O stretching frequencies depend, not only on the lithium coordination (tetrahedral or octahedral) as suggested in previous papers [7, 8], but also on the very structure of the compound [9].

Thus, we must consider the possible empty sites of the host lattice. In the BAsO_4 space group $I\bar{4}$, we have two empty sites with a two-fold multiplicity, namely (2b) and (2d) which are thus possible candidates for accommodating the lithium cation.

Starting from the unit cell parameters and the oxygen positions in BAsO_4 , we have calculated the possible Li-O distances for the (2b) and (2d) sites. Locating lithium in (2d) leads to unacceptable short distances of 0.136 and 0.164 nm. Locating lithium in (2b) gives four 0.2085 nm Li-O distances (plus four 0.2800 nm distances, which are too long to deserve further consideration), which are quite compatible with the tetrahedral coordination of lithium.

Assuming now the localization of lithium in (2b), the factor group analysis leads to two lithium translational modes (1 B + 1 E), both infrared and Raman

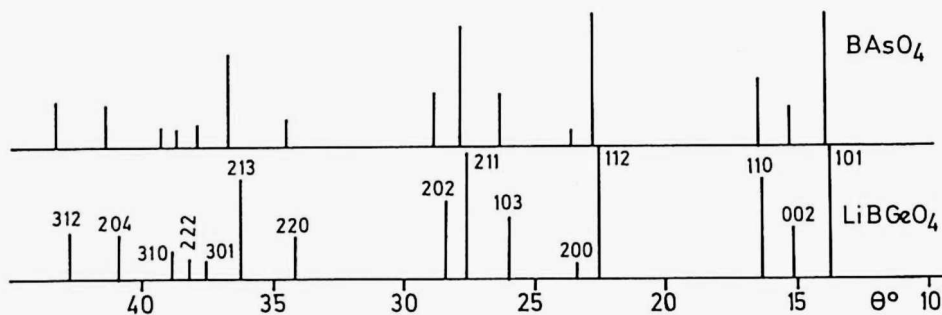


Figure 3 X-ray powder diagrams of BAsO_4 and LiBGeO_4 .

active. One of these is undoubtedly the 300 cm^{-1} band, with its large ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic shift (Table I). The second one has not been identified, but it should be pointed out that the lithium translations belong to the same representations (B and E) as other lattice modes with, as a consequence, the possibility of a more or less severe mixing.

During the study of some borosilicates $\text{M}^+\text{BSi}_2\text{O}_6$ with a pollucite-like structure, Richerson and Hummel [10] reported the impossibility to synthesize the corresponding borogermanate CsBGe_2O_6 (in contrast with the existence of the analogous silicates and germanates $\text{M}^+\text{M}^{\text{III}}\text{Si}_2\text{O}_6$ (Ge_2O_6), with $\text{M}^{\text{III}} = \text{Al, Ga}$ or Fe). This may be explained by the large difference in the sizes of the BO_4 and GeO_4 groups, which should be statistically distributed over the tetrahedral sites of a pollucite-like structure. This size constraint, however, does not exist if boron and germanium are located on non-equivalent crystallographic sites. It is thus suggested that, whenever borogermanates do exist, their structure must be characterized, either by different coordinations of boron and germanium (e.g. BO_3 and GeO_4), or by an ordered distribution of BO_4 and GeO_4 tetrahedra.

In conclusion, LiBGeO_4 and BaAsO_4 are most probably isostructural. This implies an ordered distribution of BO_4 and GeO_4 tetrahedra in a cristobalite-like lattice, whereas the Li^+ cations are probably localized in tetrahedral voids of the lattice. No ionic conductiv-

ity has been detected between 300 and 600 K. The crystal-to-glass transition is characterized by the partial transformation of BO_4 into BO_3 groups.

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