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# An infrared spectroscopic study of $\text{Li}_2\text{B}_4\text{O}_7$

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## Abstract

The temperature evolution of the infrared powder spectra of lithium tetraborate  $\text{Li}_2\text{B}_4\text{O}_7$  has been measured in the infrared region 50–1600  $\text{cm}^{-1}$  and over a temperature range between 20 K and 680 K. In contrast to the sharp B–O bands, the Li-related bands in the region between 300  $\text{cm}^{-1}$  and 510  $\text{cm}^{-1}$  are rather broad even at 20 K. With increasing temperature these bands show a stronger thermal response than in the higher-frequency region: the bands at 350  $\text{cm}^{-1}$  and 424  $\text{cm}^{-1}$  shift significantly in frequency and become very broad above 500 K. The 508  $\text{cm}^{-1}$  band appears to split into two individual bands near 500 K. The broadening of the Li-related bands is probably due to the thermally induced Li disorder. The temperature dependence of the B–O bending and stretching vibrations does not show clear evidence of structural phase transitions in  $\text{Li}_2\text{B}_4\text{O}_7$  occurring in the temperature range between 20 K and 680 K.

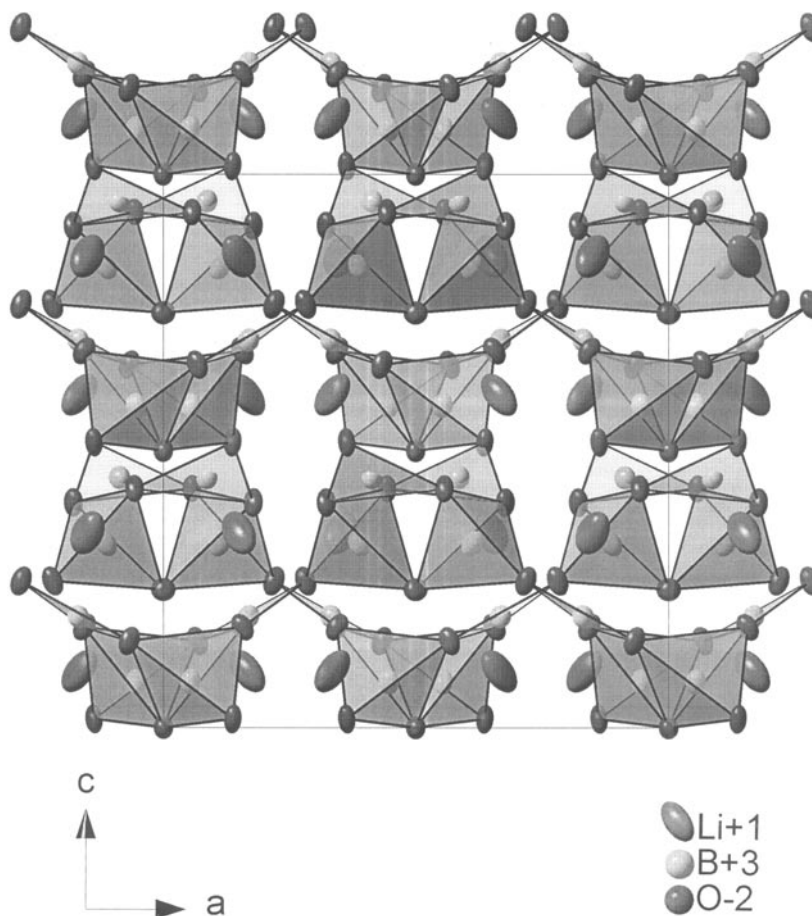
## 1. Introduction

In recent years, much research has focused on borate materials because of their potential technical applications [1]. Lithium tetraborate,  $\text{Li}_2\text{B}_4\text{O}_7$  (abbreviated hereafter as LTB), one such borate material, has possible applications in piezotechnology, acoustoelectronics and nonlinear optics [2–8] (e.g., as a substrate material for surface acoustic wave (SAW) devices [2, 3] or a frequency-conversion material for fourth- and fifth-harmonic generation from a high-power Nd:YAG laser [9], and Ag- or Cu-doped LTB crystals are widely used as thermoluminescence dosimeters [10]).

The crystal structure of LTB has been determined by Krogh-Moe [11, 12]. More accurate bond lengths and angles have been determined and refined by Natarajan *et al* [13] and Radaev *et al* [14]. Its structure at room temperature is tetragonal with the space group  $I4_1cd$  ( $C_{4v}^{12}$ ) and point group  $4mm$  with the polar axis along the crystallographic  $c$ -axis. The lattice constants

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are  $a = 9.477 \text{ \AA}$  and  $c = 10.286 \text{ \AA}$  [11]. The structure with eight formula units of  $\text{Li}_2\text{B}_4\text{O}_7$  contains a basic building block of two  $\text{BO}_4$  tetrahedra linked by a common oxygen atom, forming a  $\text{B}_2\text{O}_7$  group (figure 1). Boron atoms forming planar  $\text{BO}_3$  triangles join these to yield a network of  $\text{B}_4\text{O}_7$  groups. The lithium atoms lie in a channel of very distorted tetrahedra.



**Figure 1.** The crystal structure of  $\text{Li}_2\text{B}_4\text{O}_7$ . The basic building block of the structure is two  $\text{BO}_4$  tetrahedra linked to form a  $\text{B}_2\text{O}_7$  group. Boron atoms forming planar  $\text{BO}_3$  triangles join these to yield a network of  $\text{B}_4\text{O}_7$  groups. The lithium atoms lie in a channel of very distorted tetrahedra.

Although extensive investigations have focused on the physical properties of LTB, experimental results have indicated controversial anomalies regarding the temperatures where they occur and concerning their physical origins, especially whether they are related to structural phase transitions. For example, numerous thermal scintillations were observed in LTB not excited by hard quanta, with temperature varying in the range between 80 and 250 K [15]. Dilatometric studies [16] point to the possible existence of a large number of phase transitions in the above-mentioned temperature range. Unusual behaviours of LTB at low temperatures have also been observed in x-ray diffraction studies [17, 18]. A new phenomenon has been revealed in LTB, which consists in a phase transition into an incommensurate phase under the influence of thermal cycling [19, 20]. Anisimova *et al* [21] attribute the observed memory effect exhibited by the elastic modulus of LTB to incommensurate modulation in

the crystal. Anomalies in the temperature variation of the sound velocity and the attenuation of sound were found at 318, 215, 125 and near 75 K [22, 23]. The same authors also note anomalies at 215, 125 and 75 K as seen in Raman spectroscopy.

Similar confusion exists for observations at high temperatures. From the results of elastic measurements of compliance coefficients  $S_{11}^E$  ( $S_{11}^D$ ) and  $S_{22}^E$  ( $S_{22}^D$ ), Maeda *et al* [24] have concluded that an anomaly at 375 K is caused by a phase transition. They suggested that LTB has a symmetry lower than tetragonal. Bodnar [25] has found a jump-like variation of the refractive indices of LTB at high temperatures and regarded it as a combined result of the pyroelectric effect and incommensurate modulation. Recently, Kushnir *et al* [26] claimed to have demonstrated the existence of a Devil's staircase over the whole range under investigation, 290–480 K, a hysteresis character of the birefringence under cycling of temperature and a pronounced thermo-optical memory effect. Furusawa *et al* [27] have observed temperature oscillations in the second-harmonic intensity, accompanied by a global decrease of this intensity with temperature increasing from room temperature up to 800 K. Capacitance–voltage ( $C$ – $V$ ) analysis was performed in the temperature range from 573 K to 713 K in order to observe the ferroelectric characteristics of  $\text{Li}_2\text{B}_4\text{O}_7$  single crystal [28]. Furthermore, the lattice parameters were measured from room temperature to 1073 K in order to identify any phase transition. It was confirmed that LTB is ferroelectric between room temperature and 713 K, while it was suggested [28] that a phase transition existed near 773 K from the temperature dependencies of the lattice parameters. Investigations of piezoelectric and elastic properties of  $\text{Li}_2\text{B}_4\text{O}_7$  single crystal by Jung *et al* [29] did not show any phase transition between room temperature and 523 K, as reported previously [24].

The objectives of this study were twofold. Firstly, we investigated whether the reported anomalies at low and high temperatures are related to structural phase transitions. Secondly, we wished to understand the role played by Li atoms in the thermal behaviour at high temperatures. Hard-mode spectroscopy was employed in this study, as it has been found to be a useful and sensitive tool for investigation of structural change [30].

## 2. Experimental procedure

The single crystals of LTB used in this study were grown in the [100] and [001] directions by the Czochralski method in air from a stoichiometric melt. The quality and perfection of the single crystals, which are transparent, colourless and bubble-free, were confirmed by means of x-ray diffraction studies, Laue diffraction patterns and topographs. Crystals of LTB were crushed and ball milled in an agate mortar in a Spex Micro ball mill for 20 minutes. Three types of pellet were used for the different frequency ranges. KBr was used for the region 500–1600  $\text{cm}^{-1}$ , CsI for 200–700  $\text{cm}^{-1}$  and polyethylene for 50–300  $\text{cm}^{-1}$ .

The infrared spectra were recorded under vacuum at temperatures between 20 K and 680 K by using a Bruker 113V spectrometer. For high-temperature experiments, the specimen was positioned inside a cylindrical platinum-wound furnace. The temperature was measured using a Pt/PtRh thermocouple, which was pressed against the sample. A Eurotherm 815 instrument was used to control the temperature. The temperature stability was better than 1 K. Low-temperature spectra were recorded with the sample pellets mounted inside a closed-cycle Leybold cryostat. A copper mesh was kept in direct contact with the pellet in order to ensure good thermal contact between the sample and cooling finger.

A liquid-nitrogen-cooled MCT detector was used for the mid-infrared (MIR) and a room temperature DTGS detector for the far infrared (FIR). The instrumental resolution was set to 1 or 2  $\text{cm}^{-1}$  for the MIR and 2  $\text{cm}^{-1}$  for the FIR. Spectra were recorded in runs lowering and increasing temperature and the spectra obtained from heating and cooling runs are similar.

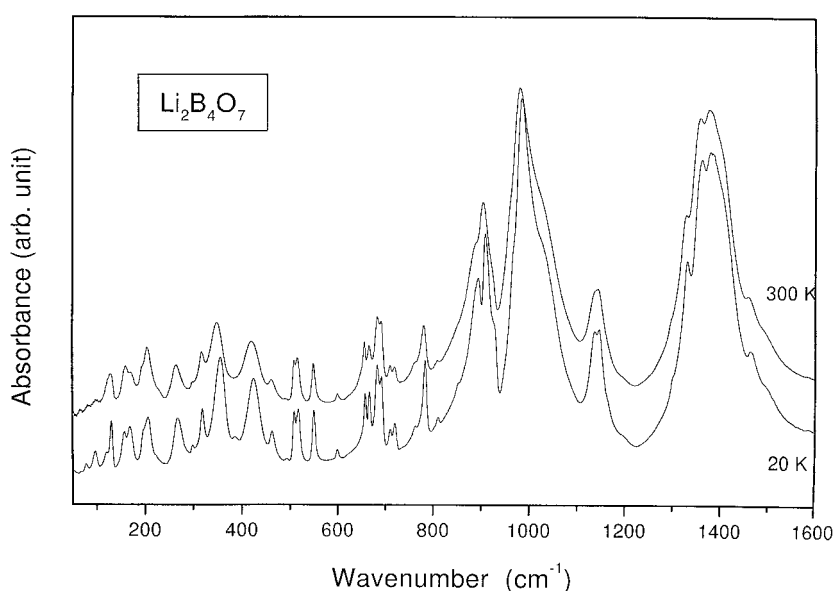
### 3. Results

From factor group analysis for the structure of LTB, it is found that the normal vibrational modes can be represented as [31]

$$\Gamma = 19A_1 + 19A_2 + 19B_1 + 19B_2 + 40E.$$

Among these,  $A_2$  is infrared active,  $A_1$ ,  $B_1$  and  $B_2$  are Raman active and  $E$  is both infrared and Raman active. The two acoustic modes are  $A_1$  and  $E$  modes. There are 57 infrared modes.

Figure 2 shows the infrared absorption spectra of LTB at 300 K and 20 K recorded in the frequency region between  $50\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ . The infrared spectra of LTB are dominated by bands between  $800\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  and between  $1200\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ . The infrared bands between  $1200$  and  $1500\text{ cm}^{-1}$  are due to the B–O stretching from the  $\text{BO}_3$  group and the B–O stretching bands of the  $\text{BO}_4$  group are in the region from  $800\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$  [32, 33]. The infrared bands between  $600$  and  $800\text{ cm}^{-1}$  are mainly due to B–O bending [34].



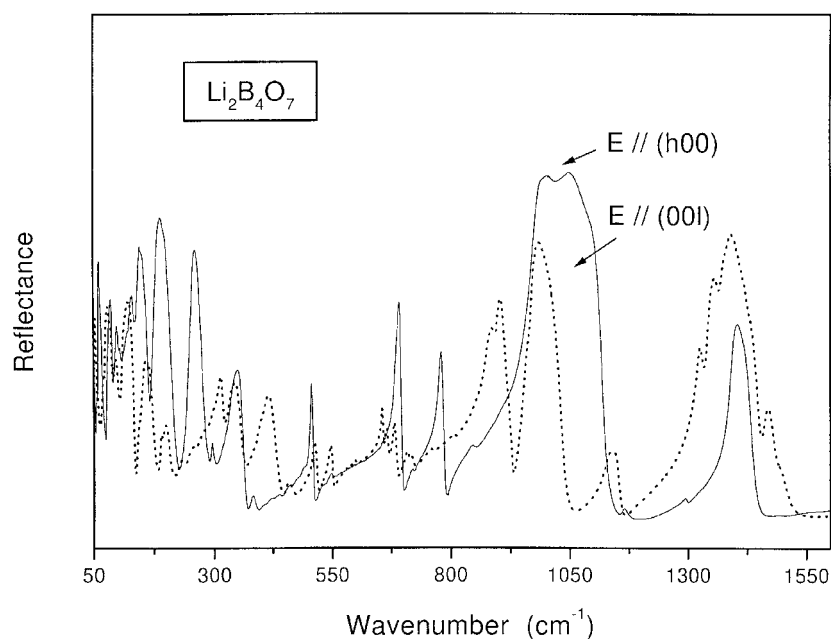
**Figure 2.** The infrared absorption spectra of  $\text{Li}_2\text{B}_4\text{O}_7$  at 300 K and 20 K in the region from  $50\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$ .

Extensive infrared studies of Li-containing compounds indicate that peaks in the region  $300\text{--}510\text{ cm}^{-1}$  are characteristic of Li coordinated by four O nearest neighbours [35]. The peaks at  $\sim 420\text{ cm}^{-1}$  for the  $\text{LiBO}_2$  and  $\text{Li}_2\text{B}_4\text{O}_7$  crystals have previously been assigned to Li [36]. The thermal behaviours of these Li bands may be directly associated with the Li mobility or Li disorder at high temperatures.

42 modes are observed in the frequency region between  $50\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  at 20 K; they are summarized in table 1. Figure 3 shows polarized infrared reflection spectra of LTB at room temperature recorded between  $50\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ . As can be seen, the infrared spectra show strong polarization effects. Examination of the single-crystal infrared reflection spectra of  $\text{Li}_2\text{B}_4\text{O}_7$  reveals that the infrared bands at  $355\text{ cm}^{-1}$  and  $424\text{ cm}^{-1}$  are due to vibrations along the  $[00l]$  direction, i.e. the crystallographic  $c$ -axis of the crystal. One expects to see significant changes of the spectral features of these bands if the Li atoms hop along the  $c$ -axis at high temperatures.

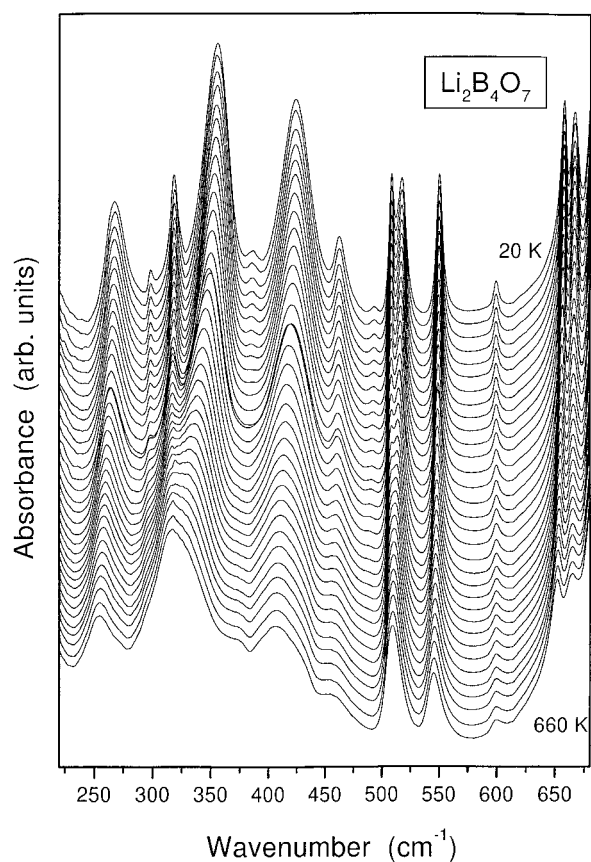
**Table 1.** Infrared absorption bands of  $\text{Li}_2\text{B}_4\text{O}_7$  at 20 K. The peak frequency,  $\omega$ , is in  $\text{cm}^{-1}$ .

No	$\omega$	No	$\omega$	No	$\omega$
1	98	15	462	29	854
2	122	16	493	30	895
3	130	17	508	31	909
4	158	18	518	32	929
5	169	19	550	33	986
6	196	20	600	34	1028
7	206	21	667	35	1137
8	223	22	683	36	1148
9	267	23	693	37	1198
10	298	24	710	38	1302
11	318	25	720	39	1332
12	355	26	762	40	1361
13	387	27	784	41	1381
14	424	28	810	42	1465

**Figure 3.** The infrared reflection spectra of  $\text{Li}_2\text{B}_4\text{O}_7$  at 300 K in the region from  $50 \text{ cm}^{-1}$  to  $1600 \text{ cm}^{-1}$ .

Figures 4 and 5 show the temperature evolution of the infrared powder absorption spectra in the region  $225\text{--}675 \text{ cm}^{-1}$  and in the region  $600\text{--}1600 \text{ cm}^{-1}$ , respectively. The infrared bands show sharpening in width, shift in frequency and increase in intensity with decreasing temperature. The infrared bands between  $600 \text{ cm}^{-1}$  and  $1600 \text{ cm}^{-1}$ , which are mainly due to internal  $\text{BO}_4$  tetrahedra and  $\text{BO}_3$  octahedra, exhibit weak frequency shifts and lines broadening with increasing temperature.

On the other hand, the bands between  $300 \text{ cm}^{-1}$  and  $510 \text{ cm}^{-1}$  show stronger thermal responses than bands at higher frequencies. These bands are much broader at high temperature

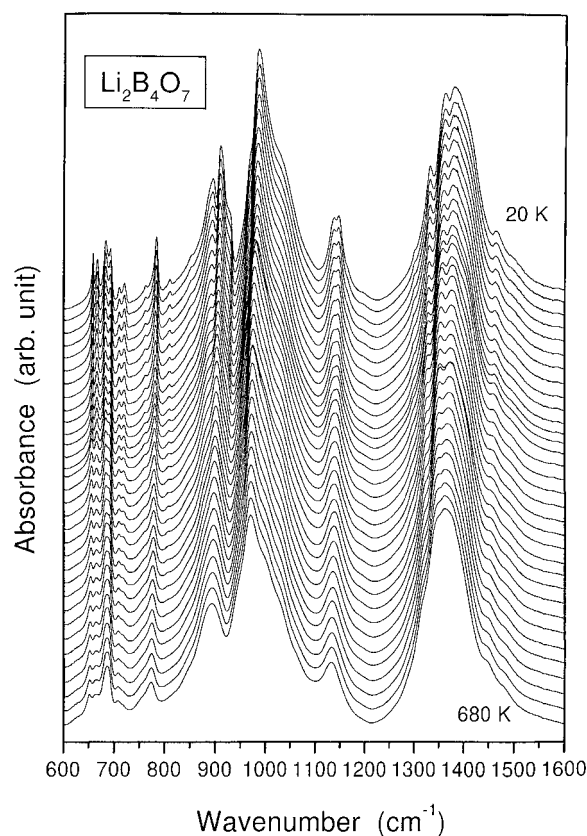


**Figure 4.** Temperature evolution of the infrared powder absorption spectra in the region from  $225\text{ cm}^{-1}$  to  $675\text{ cm}^{-1}$  for  $\text{Li}_2\text{B}_4\text{O}_7$  between 20 K and 660 K. The temperature interval is 20 K. CsI pellets were used.

and some of them become almost invisible on heating above 500 K. The bands at  $350\text{ cm}^{-1}$  and  $420\text{ cm}^{-1}$  shift significantly in frequency and become very broad above 500 K. Near 500 K, the bands at  $320\text{ cm}^{-1}$  and  $508\text{ cm}^{-1}$  appear to split into two. With changing temperature the B–O bending bands between  $600\text{--}800\text{ cm}^{-1}$  and the B–O stretching bands in the higher-frequency region do not show large frequency shifts or unusual broadening that may suggest significant structural changes. In contrast to the sharp B–O bands, the bands in the region between  $300$  and  $510\text{ cm}^{-1}$  are rather broad even at 20 K, particularly the bands at  $424\text{ cm}^{-1}$  and  $320\text{ cm}^{-1}$ . The cause for this broadening is thought to be the freezing of a highly disordered distribution of Li.

#### 4. Discussion

Let us look at whether the reported anomalies [15–27] are related to structural changes, i.e. whether they really correspond to structural phase transitions. The information available indicates that these anomalies may not correspond to a real displacive phase transition involving the whole framework for the following reasons. Firstly, no anomalies were detected in the high-frequency region, which is mainly related to the  $\text{BO}_4$  framework. Figure 6 shows the

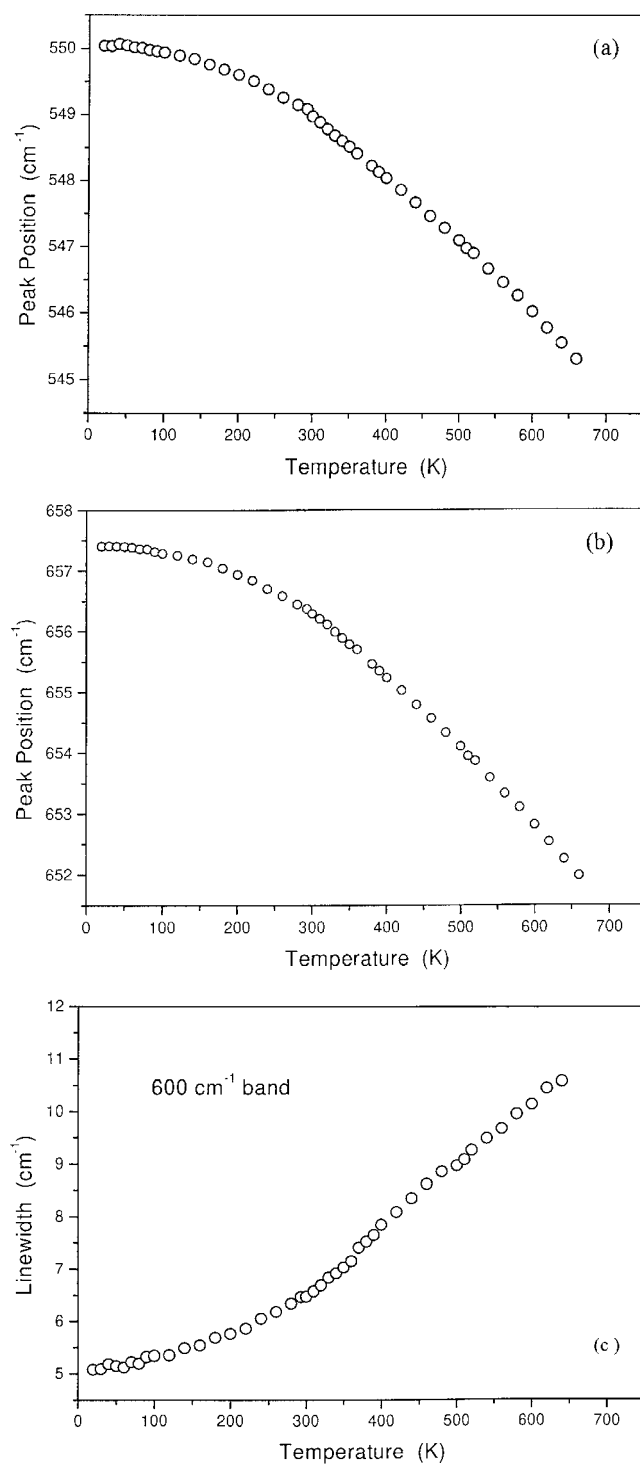


**Figure 5.** The infrared spectra in the region from  $600\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$  for  $\text{Li}_2\text{B}_4\text{O}_7$  over the temperature range between 20 K and 680 K. The temperature interval is 20 K. KBr pellets were used.

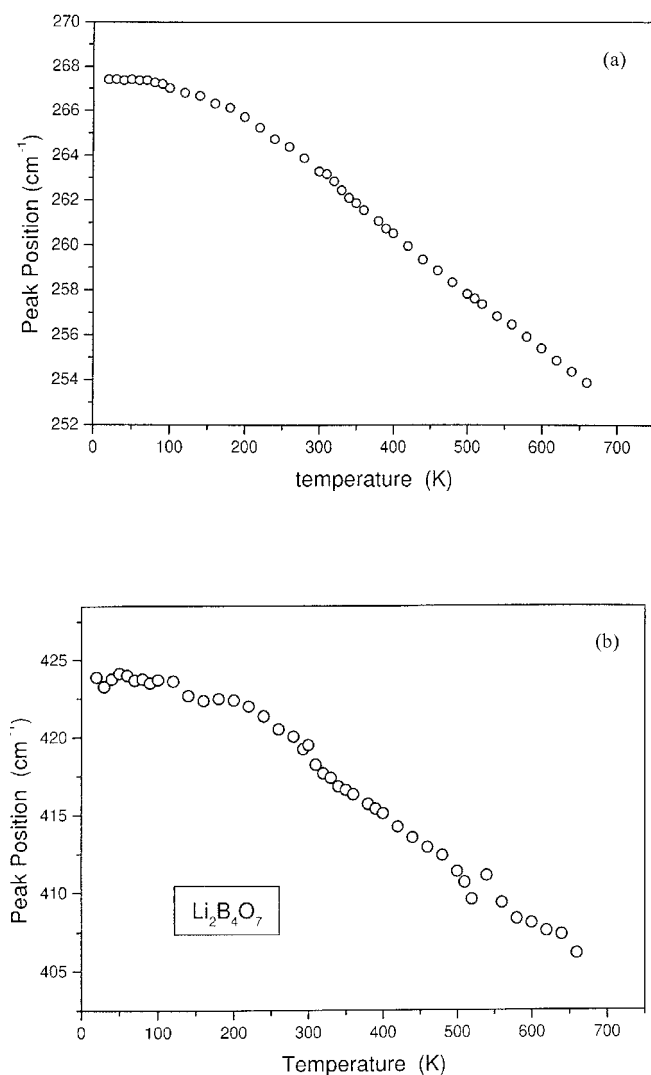
peak profile analysis of the infrared bands at  $550\text{ cm}^{-1}$  (figure 6(a)) and  $657\text{ cm}^{-1}$  (figure 6(b)) and the temperature dependence of the linewidth of the  $600\text{ cm}^{-1}$  band (figure 6(c)). It is seen that the B–O bending bands at  $550\text{ cm}^{-1}$  and  $657\text{ cm}^{-1}$  exhibit the normal thermal behaviour at high and low temperatures, i.e. a linear temperature dependence at high temperatures and saturation at low temperatures. The temperature dependence of the linewidth of the  $600\text{ cm}^{-1}$  band also shows ‘normal’ behaviour. The same is true in the case of the low-frequency bands at  $267\text{ cm}^{-1}$  (figure 7(a)) and  $424\text{ cm}^{-1}$  (figure 7(b)). With this in mind, we conclude that there is no clear evidence for structural phase transitions in the temperature region between 20 and 680 K from the point of view of symmetry breaking. Our conclusion is in agreement with Raman data given by Paul and Taylor [31], which show that Raman spectra obtained at 295, 323 and 373 K are similar to those at 100 K. Also, the lattice parameters measured between 80 and 450 K using x-ray diffractometry [37] show no indication of a phase change and results on the piezoelectric and elastic properties [29] show that there is no indication of a phase transition from room temperature up to 523 K.

One can see that with increasing temperature the weak peak near  $382\text{ cm}^{-1}$  at 20 K weakens further and finally becomes undetectable in powder absorption spectra above 220 K (figure 4). However, its appearance in the polarized spectrum with  $\mathbf{E} \parallel c$  measured at room temperature (figure 3) suggests that this mode is still IR active above 220 K and its weak





**Figure 6.** Peak profile analysis of the infrared bands at 550  $\text{cm}^{-1}$  (a) and 657  $\text{cm}^{-1}$  (b) and the temperature dependence of the linewidth of the 600  $\text{cm}^{-1}$  band (c).



**Figure 7.** Temperature dependences of the bands at  $267\text{ cm}^{-1}$  (a) and  $424\text{ cm}^{-1}$  (b).

intensity made it appear to have vanished. Therefore, its absence from powder absorption spectra above 220 K is not related to structural changes. The disappearance or undetectability of the  $493\text{ cm}^{-1}$  band in the spectra above 400 K might have a similar cause. An anomaly was observed near 500 K and it was characterized by a possible band split near  $510\text{ cm}^{-1}$  at a temperature near 500 K as shown in figure 4. It appears that the  $508\text{ cm}^{-1}$  band vanished above 500 K because curve-fitting results favour only one peak. The integrated absorbance from  $500\text{ cm}^{-1}$  to  $538\text{ cm}^{-1}$  did not show anomalies between 20 K and 680 K. It is also hard to envisage that during a transition those phonon modes in the frequency region above  $600\text{ cm}^{-1}$  related to the framework built from  $\text{BO}_3$  and  $\text{BO}_4$  groups failed to 'see' the structural change.

Some authors attribute the observed anomalous behaviour of many physical properties to incommensurate modulations in the crystal. Our data do not completely rule out the possibility of the existence of the incommensurate phase transition reported previously. However, other

possible causes for these reported anomalies at low and high temperatures are structural defects [38–40], the presence of OH [41], strong anisotropy, incomplete freezing of Li disorder and possible structural distortions caused by thermally induced compression. Application of other methods such as TEM and neutron diffraction investigation is desirable to clarify the controversy.

The broadening of Li-related bands is probably due to the thermally induced Li disorder. To understand why Li ions become disordered let us look more closely at the crystal structure of LTB. As we can see in figure 1, the main building block is constructed of two  $\text{BO}_4$  tetrahedra and two planar  $\text{BO}_3$  triangles linked by a common oxygen atom [11]. The framework forms channels along the  $c$ -axis, where  $\text{Li}^+$  ions are weakly confined in distorted tetrahedra. It is clear that the B–O complex remains motionless while Li ions start their movement with increasing temperature, which leads to the broadening of Li-related bands. Indeed, anisotropy has been observed in the ionic conductivity and the results suggest that Li ions can move easily along the (001) plane [42, 43]. This compound exhibits high ionic conductivity and rather low values of the activation energy ( $\sim 0.4$ – $0.5$  eV) [42, 43]. Thus it could belong to the group of superionic conductors. Dynamic disorder of one (or more) sublattice(s) of the crystal is the distinguishing feature of ionically conducting solids [44, 45]. The disorder could be a result of either a temperature increase alone or an order–disorder structural phase transition. In the first case the process of ion disordering has a monotonic character over the entire temperature range while in the second case ion disordering usually takes place in the vicinity of the corresponding phase transition point ( $T_c$ ) [46]. In some cases an order–disorder phase transition in superionic conductors is not observed with a temperature decrease down to almost 0 K. As a result, the high-temperature dynamic disorder gradually transforms to a low-temperature static disorder [47], in analogy to glass formation upon cooling of certain liquids. Perhaps this is the case for LTB, because the Li-related bands are rather broad even at 20 K, i.e. the high-temperature disorder due to Li-ion motion is frozen at low temperature. The results indicating crystallization of the mobile-ion subsystem are not yet confirmed.

## 5. Conclusions

Infrared spectroscopic work on lithium tetraborate  $\text{Li}_2\text{B}_4\text{O}_7$  has been systematically performed in the infrared region  $50$ – $1600$   $\text{cm}^{-1}$  and over the temperature range between 20 K to 680 K. We can conclude that there is no clear evidence for any structural phase transitions in LTB crystals between 20 and 680 K from the point of view of symmetry breaking. The temperature dependences of the B–O bending and stretching vibrations exhibit normal thermal behaviour. The broadening of the Li-related bands in the region  $300$ – $510$   $\text{cm}^{-1}$  is probably due to the thermally induced Li disorder.

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