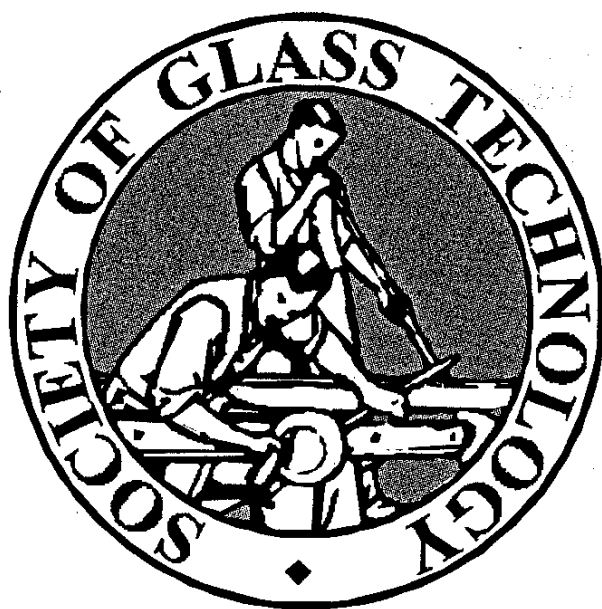


BORATE GLASSES, CRYSTALS & MELTS

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A VIBRATIONAL SPECTROSCOPIC STUDY OF ALKALINE EARTH BORATE GLASSES

Yiagos D. YIANNOPOULOS, Efstratios I. KAMITSOS,
Georgios D. CHRYSSIKOS & John A. KAPOUTSIS
*Theoretical and Physical Chemistry Institute, NHRF, 48, Vass.
Constantinou Ave., 116 35 Athens, GREECE*

The study of the mid infrared and Raman spectra of Ca-, Sr- and Ba-borate glasses has shown that their network is composed of borate arrangements containing $B\text{O}_4^-$ tetrahedra (O =bridging oxygen atom) and metaborate, $B\text{O}_2\text{O}^-$, triangular units. The fraction of four-coordinated boron atoms, N_4 , was obtained and found to exhibit a maximum at compositions depending on the type of alkaline earth cation. For fixed metal oxide contents, N_4 increases with increasing metal ion size, a trend opposite to that exhibited by alkali borate glasses. Mg-borates were found to have the lowest N_4 values, and this was shown to originate from the disproportionation of the borate network to boroxol rings and pyroborate species. The analysis of the far infrared profiles suggests the presence of two types of sites hosting alkaline earth cations, i.e. sites which are well organised, or 'crystal-like', and sites which are less organised.

1. INTRODUCTION

The structure and properties of oxide glasses depend strongly on the nature and concentration of the constituent oxides. The effect of alkaline earth cations on the structure of borate glasses, $x\text{MO} \cdot (1-x)\text{B}_2\text{O}_3$, has been studied extensively by Bray and co-workers using ^{11}B NMR spectroscopy [1-5]. It was shown that at low MO contents the alkaline earth cations behave like alkali modifier ions and the fraction of four-coordinated boron atoms, N_4 , follows the $N_4 = x/(1-x)$ law. At higher MO contents the M^{2+} ions start gaining network forming ability, and this is manifested by lowering their coordination number with oxygen atoms. As an effect the conversion rate of boron coordination from three to four is reduced, this phenomenon being particularly strong in Mg-containing borate glasses [4]. Besides their glass modifying/forming properties, MO oxides can induce also a change of oxygen coordination number from two to three. This was reported to be the case of $\text{SrO}-\text{B}_2\text{O}_3$ glasses with compositions in the range $0.33 < x \leq 0.41$ [3].

As shown for alkali borate glasses, Raman and mid infrared spectroscopies are very sensitive probes of the structures assumed by the borate network [6-9], while far infrared spectroscopy can reveal the nature of interactions between the alkali metal ions and their sites [10-13]. It is the strength of such interactions

that determines the nature of M–O bonding and thus the glass-modifying/forming properties of metal oxide.

In comparison to alkali borates, a limited number of vibrational studies has been published for alkaline earth borate glasses [7,14-17]. In this work we report some characteristic results of a systematic Raman and infrared reflectance study of glasses in the systems $x\text{MO} \cdot (1-x)\text{B}_2\text{O}_3$, $\text{M}=\text{Mg}$, Ca , Sr and Ba , in an attempt to quantify the effect of M^{2+} on glass structure and to investigate the nature of M–O bonding as a function of metal oxide content.

2. EXPERIMENTAL

Alkaline earth borate glasses were prepared from stoichiometric mixtures of anhydrous B_2O_3 and metal carbonates ($\text{M}=\text{Sr}$, Ba), or metal oxides ($\text{M}=\text{Mg}$, Ca). The thoroughly mixed batches were melted in platinum crucibles for about half an hour in the temperature range 1100-1300°C. Glasses were obtained by quenching the melt between two polished copper blocks. The glass forming regions found in this work are given in Table 1, where they are compared with those determined for alkali borate glasses [18].

It is evident that the glass forming region becomes wider as the cation size increases. The lower MO content for glass formation is set by the onset of phase separation, while crystallization processes determine the upper MO limit. The difference in glass forming ability between alkaline earth and alkali metal oxides can be understood in terms of the field strength of the metal cations. Because of their higher field strengths, M^{2+} cations require sites of higher anionic charge density, which can exist only in glasses of relatively high MO contents.

Infrared spectra were recorded in the reflectance mode on a Fourier-transform spectrometer (Bruker IFS 113v), and were analyzed by the Kramers–Kronig technique [19] to calculate the absorption coefficient spectra reported here. Raman spectra were measured on a Jobin-Yvon spectrometer (Ramanor HG 2S) at a 90° scattering geometry, using for excitation the 488 nm line of an argon ion laser (Spectra Physics 165).

Table 1
Glass Forming Regions of Alkaline Earth and Alkali Borate Glasses

Cation	Glass Forming Region
$x\text{MO} \cdot (1-x)\text{B}_2\text{O}_3$	
Mg	$0.45 \leq x \leq 0.55$
Ca	$0.33 \leq x \leq 0.50$
Sr	$0.20 \leq x \leq 0.47$
Ba	$0.20 \leq x \leq 0.47$
$x\text{M}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$	
Li	$0 \leq x \leq 0.75$
Na	$0 \leq x \leq 0.45$ and $0.55 \leq x \leq 0.75$
K	$0 \leq x \leq 0.45$ and $0.60 \leq x \leq 0.70$
Rb	$0 \leq x \leq 0.45$ and $0.65 \leq x \leq 0.70$
Cs	$0 \leq x \leq 0.75$

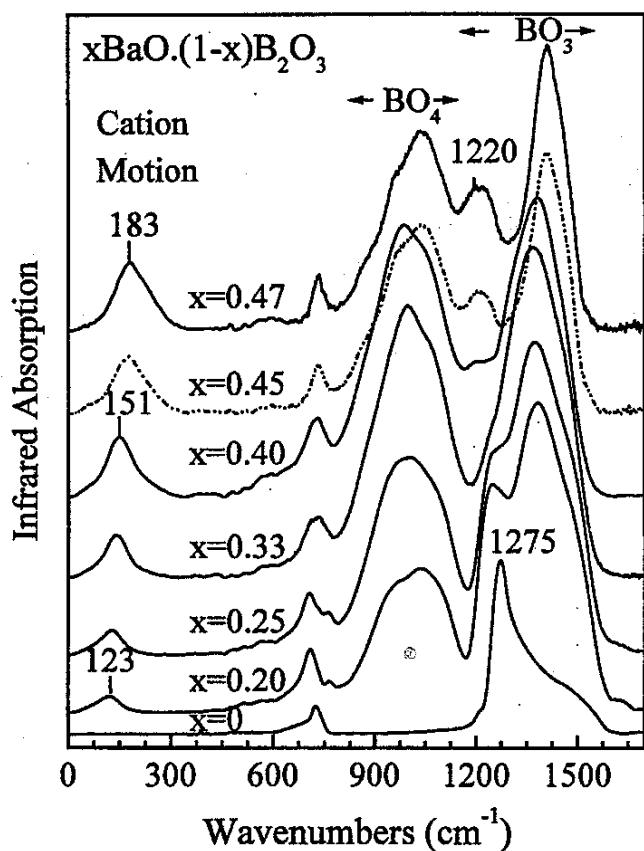


Fig. 1. Infrared Absorption Spectra of $x\text{BaO} \cdot (1-x)\text{B}_2\text{O}_3$ glasses.

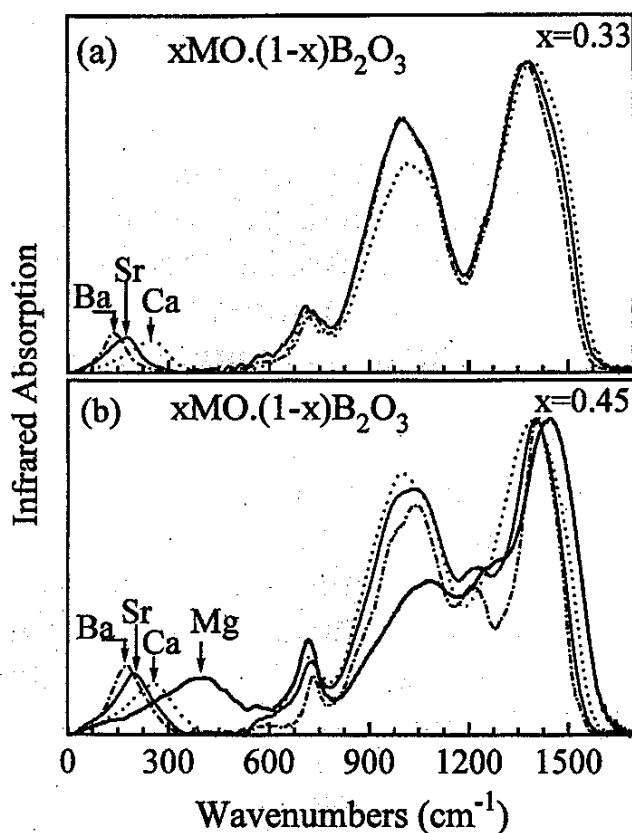


Fig. 2. Infrared Absorption Spectra of $x\text{MO} \cdot (1-x)\text{B}_2\text{O}_3$ glasses with $x=0.33$ (a) and $x=0.45$ (b).

3. RESULTS AND DISCUSSION

3.1. Effect of Alkaline Earth Oxide on the Structure of the Borate Network

Infrared absorption spectra of glasses in the barium borate system are shown in Fig. 1. The corresponding reflectivity spectra are in good agreement with those published recently by Kim et al [20]. In order to understand the effect of BaO addition on the structure of the borate network we consider the mid-infrared region ($500\text{--}1600\text{ cm}^{-1}$), where the vibrations of the boron–oxygen arrangements are active. In particular, absorption in the $800\text{--}1150\text{ cm}^{-1}$ range can be attributed to the B–O asymmetric stretching vibration of BO_4 tetrahedra, and the high frequency absorption profile ($1150\text{--}1550\text{ cm}^{-1}$) to the corresponding vibration of BO_3 triangles [19]. Therefore, the evolution of the $800\text{--}1150\text{ cm}^{-1}$ envelope with x in the range $0 < x \leq 0.40$ (Fig. 1) shows the progressive change of boron coordination number from three to four. For higher BaO contents a decrease of the relative intensity of the BO_4 absorption band is observed, signaling the formation of non-bridging oxygen (NBO) containing triangles. Indeed, the band developing at 1220 cm^{-1} can be assigned to the B–O asymmetric stretching vibration of BO_2O^- triangles in metaborate rings [19,21].

The dependence of the glass structure on the type of alkaline earth cation is illustrated in Fig. 2, where the spectra of glasses with fixed MO content ($x=0.33, 0.45$) are compared. To facilitate comparison, all spectra have been scaled at the high frequency absorption envelope. It is clear from Fig. 2 that absorption in the

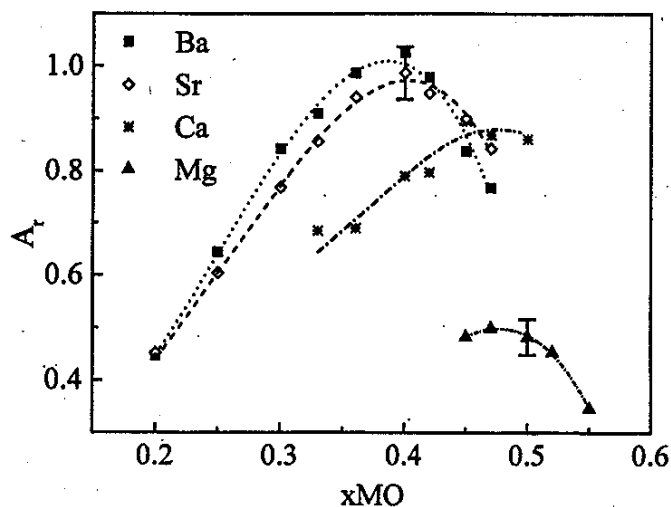


Fig.3. Relative integrated intensity $A_r=A_4/A_3$ for $xMO.(1-x)B_2O_3$ glasses. Lines through data points are drawn to guide the eye.

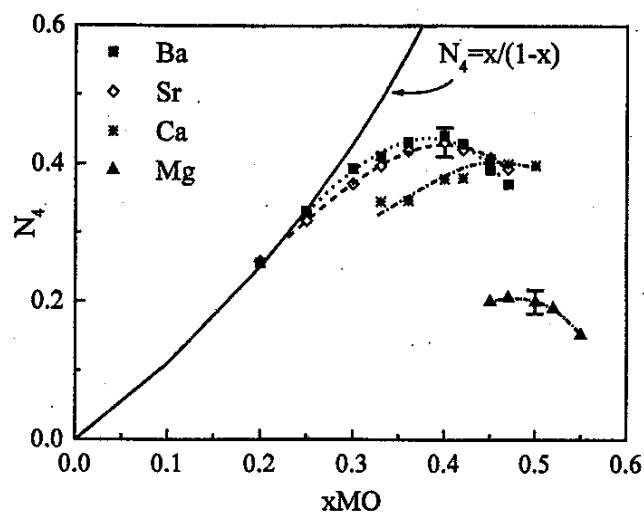


Fig.4. The fraction of four-coordinated boron atoms, N_4 , in $xMO.(1-x)B_2O_3$ glasses calculated using Eq. (1). Comparison is made with the theoretical, $x/(1-x)$, values. Lines through data points are drawn to guide the eye.

range characteristic of BO_4 tetrahedra depends on type of alkaline earth cation. To quantify the effect of alkaline earth oxide on the short-range structure of the borate network we have calculated the integrated intensity of the absorption envelopes $800-1150\text{ cm}^{-1}$ and $1150-1550\text{ cm}^{-1}$, denoted by A_4 and A_3 , respectively. The relative integrated intensity, $A_r=A_4/A_3$, is plotted in Fig. 3 versus MO content. The change of boron coordination from three to four with increasing MO content towards the metaborate composition ($x=0.50$) is illustrated very clearly in this figure. It is observed also that the MO content at which A_r exhibits its maximum value is a function of the type of alkaline earth oxide.

The relative integrated intensity, A_r , can be employed to calculate the fraction of boron atoms with fourfold coordination, N_4 , by using the expression,

$$N_4 = A_r / (\alpha + A_r) \quad (1)$$

where α is the relative absorption coefficient of boron tetrahedra versus boron triangles [22,23]. The value of α can be obtained by comparing infrared data of this work (Fig. 3) with recently published NMR results by Huebert et al [15]. Using these NMR data it can be shown that the N_4 values for binary Sr-borate glasses with $x=0.40$ and $x=0.47$ are $N_4=0.44$ and $N_4=0.39$, respectively [15]. These values and Eq. (1) give an average value of $\alpha=1.3$. Although α is expected to show a cation dependence, the lack of recent NMR data for binary Ba- and Ca-borate glasses leads us to employ the value $\alpha=1.3$ to calculate N_4 for the three Ba-, Sr- and Ca-borate glass systems. As shown in Fig. 3 Mg-borate glasses exhibit distinctly lower values of A_r , indicating that the value of α for these glasses should be calculated separately. According to Dell & Bray, $N_4=0.20$ for the $0.45MgO.0.55B_2O_3$ glass [5], giving the value $\alpha=1.9$ for Mg-borate glasses.

Using the infrared data (A_r) and the values of α obtained above, N_4 was

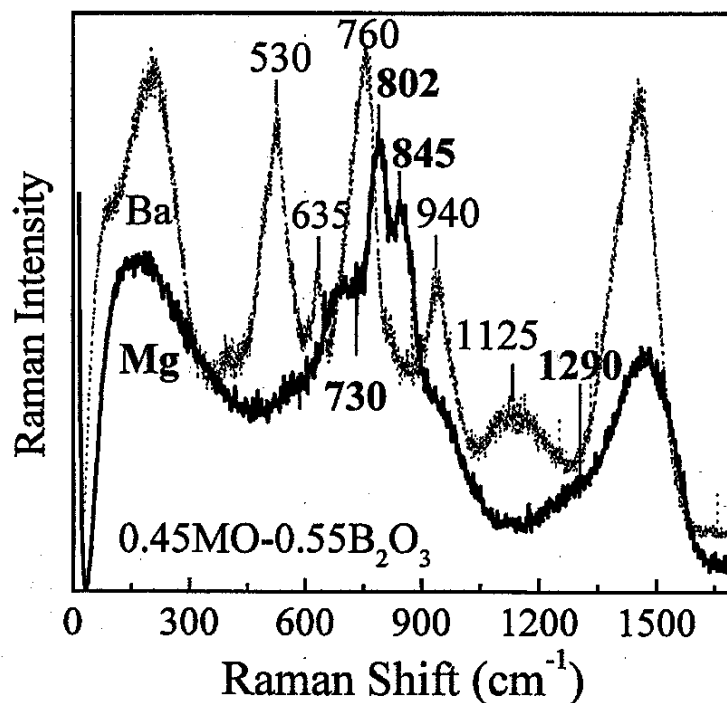


Fig. 5. Raman spectra of Ba- and Mg-borate glasses with $x=0.45$.

calculated through Eq. (1). The results are shown in Fig. 4 versus MO content and compared with the theoretical values, $x/(1-x)$. The following observations can be made; (a) for Ba- and Sr-glasses of low MO contents (up to $ca\ x=0.25$) N_4 follows the theoretical value, (b) the MO content at which N_4 attains its maximum value shifts to higher x values as the field strength of M^{2+} increases, and (c) for glasses of the same MO content N_4 decreases with increasing field strength of M^{2+} cation. It is worth noting that this trend is opposite to that found in alkali borate glasses, i.e. a decrease of N_4 from Li to Cs [21, 24].

To understand the origin of the distinctly lower N_4 values exhibited by Mg-borate glasses we compare in Fig. 5 the Raman spectra of Mg- and Ba-borate glasses with $x=0.45$.

The spectrum of the barium-borate glass shows features characteristic of borate arrangements containing $B\text{O}_4^-$ tetrahedra (bands at 530, 760 and 940 cm^{-1}) and metaborate rings, ($B_3\text{O}_6^{3-}$), (635 cm^{-1}) [25,26]. Therefore, the structure of the Ba-borate glass is consistent with the metaborate stoichiometry and can be described in terms of the isomerisation process: $B\text{O}_4^- \leftrightarrow B\text{O}_2\text{O}^-$. On the contrary, the spectrum of the Mg-borate glass reveals the presence of boroxol rings, $B_3\text{O}_4$, (802 cm^{-1}) and pyroborate species, $B_2\text{O}_5^{4-}$, (845 cm^{-1}) [16]. The coexistence of undermodified (boroxol rings) and overmodified (pyroborate dimers) species at the metaborate composition can be understood in terms of the following disproportionation reaction: $4\text{BO}_2^- \rightarrow (2/3)\text{B}_3\text{O}_4 + \text{B}_2\text{O}_5^{4-}$, where $\text{BO}_2^- = B\text{O}_4^-$ and/or $B\text{O}_2\text{O}^-$. This behavior of Mg-borate glasses is attributed to the largest field strength of Mg^{2+} ions, and is consistent with the fact that they exhibit the smallest value of N_4 and the smallest glass forming region among the rest of alkaline earth borates. This justifies also the different value of the relative absorption coefficient, α , of the Mg-borate glasses.

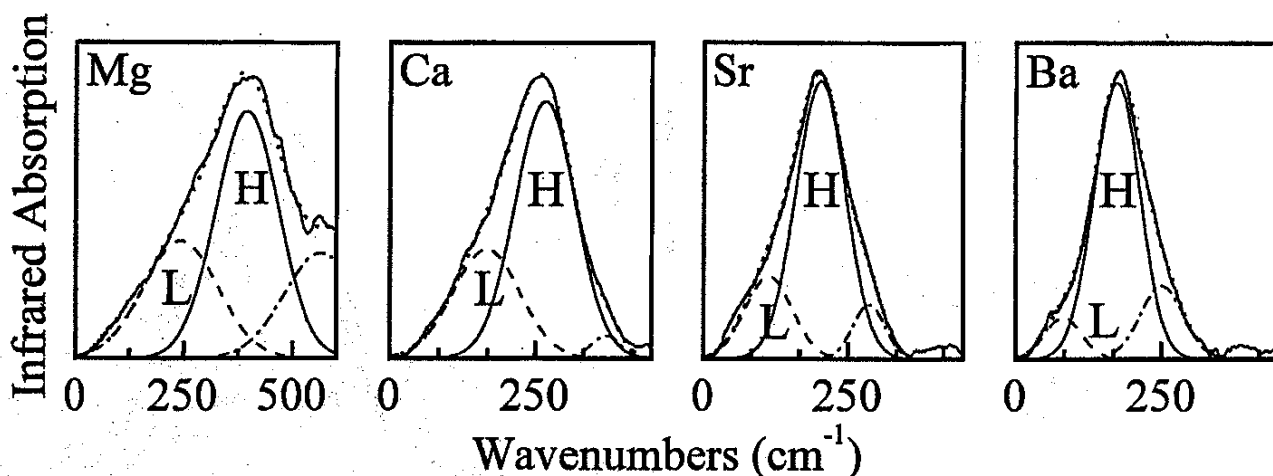


Fig. 6. Deconvoluted far infrared profiles of 0.45MO.0.55B₂O₃ glasses (M=Mg, Ca, Sr, Ba).

3.2. Far Infrared Spectra and Metal Ion / Site Interactions

As shown in Fig. 1, addition of BaO to B₂O₃ causes the appearance of a new band in the far infrared whose frequency and intensity are increasing with x. For glasses of the same MO content, the frequency of the far infrared band increases upon decreasing the mass of the alkaline earth cation (Fig. 2). Similar bands in the spectra of alkali borate glasses have been assigned to vibrations of metal ions in their equilibrium sites [10-13].

When the far infrared spectra are shown in an expanded frequency scale becomes obvious that the description of their asymmetric profiles requires deconvolution into component bands. A typical example of such spectral deconvolution into Gaussian components is shown in Fig. 6 for the 0.45MO.0.55B₂O₃ glasses. The frequencies of the two lower-frequency bands (designated by ν_L and ν_H) are plotted versus the inverse square root of the alkaline earth cation mass in Fig. 7. The linear dependence of ν_H and ν_L on $m_c^{-1/2}$ suggests that the H and L bands could be attributed to vibrations of M²⁺ cations in two types of anionic site environments in the glass (sites H and L) [21]. Besides the L and H bands, Fig. 6 shows the existence of a third band at the high frequency side. This component can be attributed to borate network modes, like the libration mode of metaborate rings [21,27].

To investigate the nature of L and H glass sites hosting M²⁺ ions, we compare in Fig. 8 the far infrared spectrum of the 0.50CaO.0.50B₂O₃ glass with that of a corresponding crystalline compound. It is observed that the H glass band forms the envelope of the infrared bands of the crystal in the range 100-350 cm⁻¹. According to Rulmont & Almou [28], the intense bands of Ca-metaborate crystal in this frequency range arise from the translational modes of Ca²⁺ cations in their sites. On these grounds we suggest that the H glass band can be attributed to vibrations of metal cations in well organized, or 'crystal-like', sites in the glass. Metal cations that do not succeed to establish such environments occupy less organized sites and may give rise to the L-type band. It is of interest to note that a similar picture was established recently from the consideration of the far infrared spectra of glassy and crystalline alkali-germanates [29].

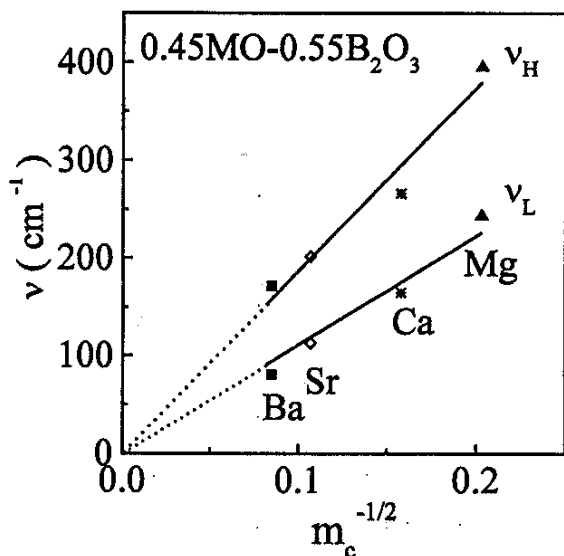


Fig. 7. Cation motion frequencies versus $m_c^{-1/2}$, where m_c is the metal ion mass. Error bars are of the size of symbols. Lines are least square fittings.

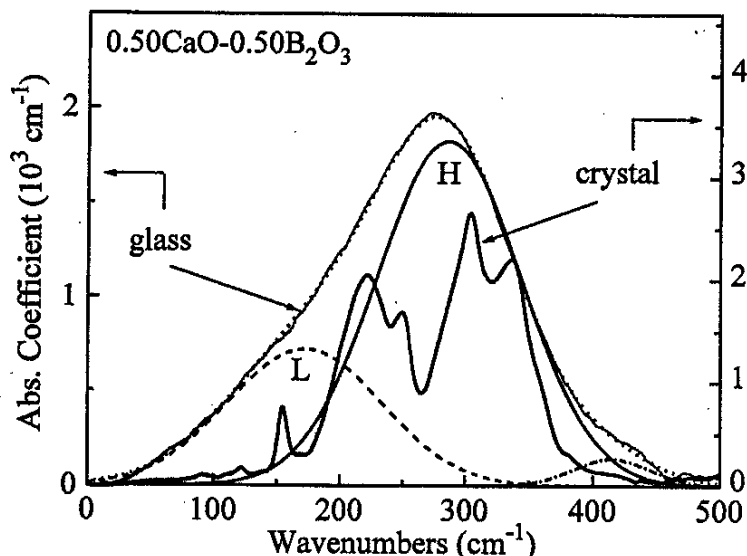


Fig. 8. Comparison of the far-infrared spectra of crystalline and glassy $0.50\text{CaO}\cdot 0.50\text{B}_2\text{O}_3$. Dashed and dotted component bands resulted from the deconvolution of the glass spectrum.

4. CONCLUSIONS

The glass-forming regions of alkaline earth borate glasses were determined and found to become wider with increasing cation size. The analysis of the infrared reflectance spectra, and comparison with recent NMR results, allowed the quantification of network structure in terms of the fraction of four-coordinated boron atoms, N_4 . It was found that N_4 increases with alkaline earth oxide content, MO, and attains maximum values at compositions depending on M^{2+} type. For glasses of the same MO content, N_4 decreases from Ba to Mg, a trend opposite to that exhibited by alkali borate glasses. The Raman spectra have shown that this effect is due to the high field strength of the Mg^{2+} cations which induce a structural disproportionation into neutral (boroxol rings) and highly charged (pyroborates) borate units. Alkaline earth cations occupy two types of site (H and L), where they vibrate with characteristic frequencies ν_H and ν_L , respectively. Comparison of the far infrared spectra of glasses and crystals of the same metal oxide content has indicated that the H-type sites are better organized than the L-type sites.

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