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NEW INSIGHTS INTO THE STRUCTURE OF ALKALI BORATE GLASSES

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The Raman and far-infrared spectra of alkali borate glasses have been measured and analysed to elucidate the role of the alkali metal cation on the glass structure. It is demonstrated that the smaller cations favor borate units containing boron tetrahedra, while non-bridging oxygens are systematically formed upon increasing alkali cation size.

Introduction

Binary alkali borate glasses have been extensively studied to elucidate the nature and the concentration of the various borate units constituting the glass network. Such studies are important for understanding the structural peculiarities of these glasses, which are manifested in the non-linear variation of most physical properties, known as the "boron anomaly" effect /1/. The key result of the previous studies was that the structure of alkali borate glasses is almost independent of the particular alkali cation, but it strongly depends on the alkali oxide content /1,2/. In this work we wish to present new Raman and far-infrared results of a comparative study of the alkali borate glass systems $\chi M_2O.(1-\chi) B_2O_3$. They demonstrate that, contrary to previous belief, the particular alkali cation plays an important role in determining the nature of the boron-oxygen units, and thus the specific glass structure.

Results and discussion

The far-infrared spectra of alkali borate glasses are dominated by broad and asymmetric bands, assigned to cation vibrations in their network sites. A detailed analysis of these spectra has been recently reported /3/. Thus, band deconvolution of the far-infrared envelopes of Li, Na and K glasses showed the presence of two component bands, originating presumably from two distributions of network sites. A similar behaviour was found to be exhibited also by Rb and Cs glasses with $\chi > 0.25$, while those of lower alkali oxide content show only one distribution of cation hosting network sites.

The results of this far-infrared study are depicted in Figure 1, where ν_H and ν_L are the frequencies of the component bands of the deconvoluted far-IR spectra. To understand such a dependence of the cation motion frequency on both composition (χ) and the nature of alkali cation we have considered all factors

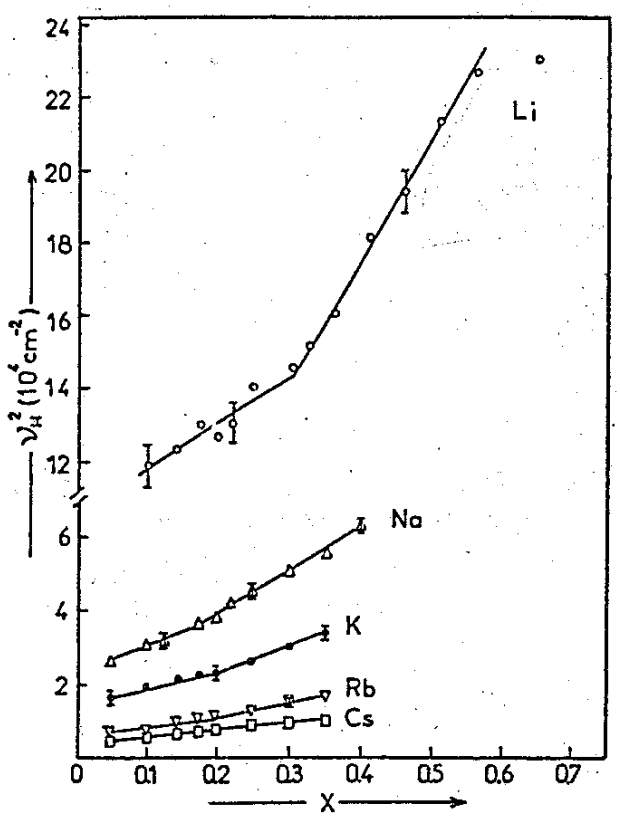

Figure 1a. Compositional dependence of ν_H^2, where ν_H is the frequency of the higher energy Gaussian component of the cation motion far-IR envelope.

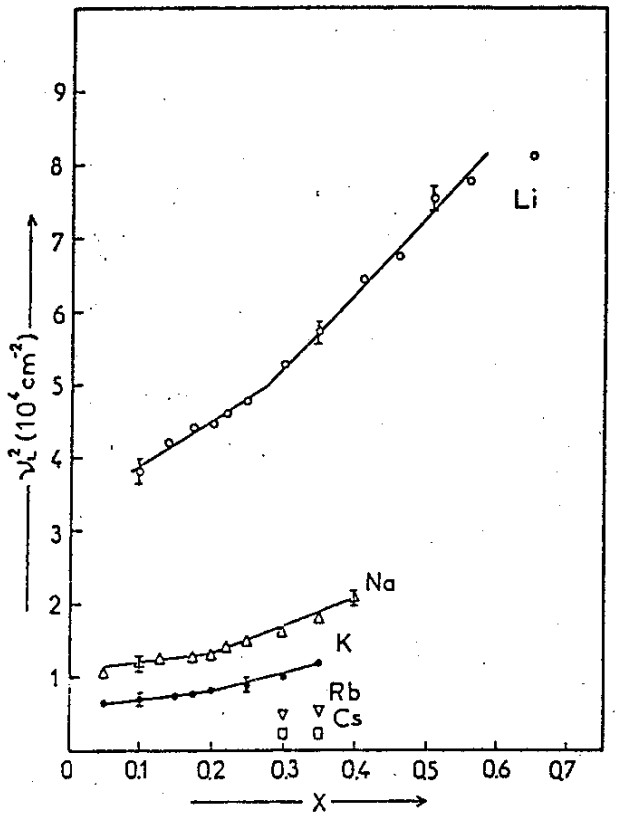

Figure 1b. Compositional dependence of ν_L^2, where ν_L is the frequency of the lower energy Gaussian component of the cation motion far-IR envelope.

affecting cation vibration, and modelled the cation-network interactions through a Born-Mayer type potential /4/. One of the main results of this analysis is the strong cation dependence of the charge density of the network sites, at the same

M_2O content. Namely, the charge density was found to decrease upon increasing alkali cation size. It was further argued /4/ that this demonstrates the preferance of the smaller alkali cations (i.e. Li^+) to $B\emptyset_4$ tetrahedra ($\emptyset$=bridging oxygen), while the bigger cations (i.e. Cs^+) favor the formation of trigonal $B\emptyset_2O$ units (O=non-bridging oxygen, NBO), through which a delocalization of the negative charge over larger network segments can take place.

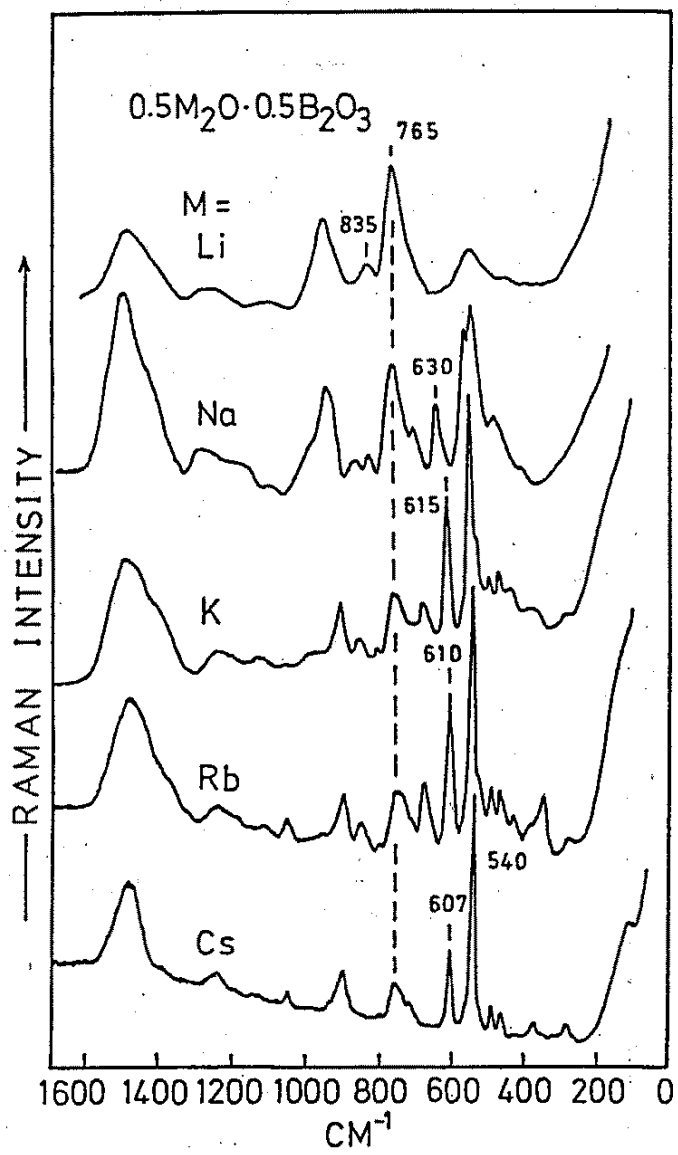

Figure 2. Raman spectra of alkali borate glasses of composition 0.5 M_2O. 0.5 B_2O_3. Glasses with M=Na, K, Rb are pseudo-binary since they contain 7, 10 and 10 mol% Al_2O_3 respectively, to bridge a discontinuous glass forming region at the metaborate composition (50 mol% M_2O). For details see:Martin S.W. and Angell C.A//J. Non-Cryst. Solids. 1984. Vol. 66. P. 429-442, and also ref/5/.

The $B\emptyset_4$ and $B\emptyset_2O$ units are parts of more complicated boron-oxygen groups, which form the borate glass network. To identify such groups, favored by each alkali cation, we have measured and analyzed the Raman spectra of alkali borate glasses over broad composition ranges. A complete Raman study will be reported elsewhere /5/. Representative Raman spectra are shown in Figure 2 for $x=0.5$ and clearly demonstrate the effect of the particular alkali cation on the glass structure. The spectrum of the Li glass exhibits its strongest band at 765 cm^{-1}, which originates from scattering of six-membered borate rings with one and/or

two $B\emptyset_4$ tetrahedra /6/. Most of these units are also responsible for the bands at 550 and 950 cm^{-1} /7/. The weak, but very characteristic band at 835 cm^{-1} indicates the presence of the highly charged pyroborate units. Thus, this spectrum shows a quite compact Li glass network, with a large concentration of $B\emptyset_4$ tetrahedra and a small content of NBO's located mainly on discrete borate units.

The spectrum of the Cs glass exhibits pronounced differences compared to that of Li glass, while those of the rest of the alkalis show an intermediate behaviour. The drastic reduction in intensity of the 760 cm^{-1} band shows a small concentration of $B\emptyset_4$ containing units in the Cs glass. On the other hand, the 607 cm^{-1} band is characteristic of the NBO-containing metaborate rings, while the strongest band at 540 cm^{-1} is indicative of the NBO-containing isolated diborate groups /6/. Thus, the Cs glass appears to contain a great number of NBO's attached to fairly large network segments, and a relatively small concentration of $B\emptyset_4$ units.

The Raman results are in agreement with the far-IR results discussed above, and also with the recent new NMR findings /8/, which have shown that the fraction of four-fold coordinated boron atoms decreases upon increasing alkali cation size. They show clearly the crucial role played by the particular alkali cation, and they are important for the structural evaluation of more complex fast ionic conducting borate glasses.

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