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LIGHT SCATTERING FROM ACOUSTIC AND LOW-FREQUENCY VIBRATIONAL MODES
IN BORATE GLASSESJ. Lorösch, M. Couzi, J. Pelous[†], R. Vacher[†] and A. Levasseur^{*}*Laboratoire de Spectroscopie Infrarouge, LA 124, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence Cedex, France**[†]Laboratoire de Spectrométrie Rayleigh-Brillouin, ERA 460, Université de Montpellier II, France**^{*}Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, France*

Résumé. - Les verres des séries $B_2O_3 - xM_2O$, avec $M = Li, Na, K, Rb, Cs, Tl$, ont été étudiés par diffusion Brillouin et Raman de basse fréquence. La variation en fonction de la concentration et de la composition de la vitesse et de l'atténuation des ondes acoustiques longitudinales et transverses, ainsi que celle du pic "Boson" ont été mesurées.

Les variations des vitesses des ondes acoustiques semblent résulter de la superposition de deux effets : le premier est lié au changement de la coordination des atomes de bore de 3 à 4 quand x augmente, et le second aux modifications structurales associées à l'encombrement stérique des cations M^+ . La fréquence du pic "Boson" présente un comportement similaire à celui de la vitesse des ondes acoustiques. L'utilisation du modèle de Martin et Brenig permet de rendre compte qualitativement des effets observés.

Abstract. - Brillouin and low frequency Raman scattering experiments have been performed on series of $B_2O_3 - xM_2O$ glasses where $M = Li, Na, K, Rb, Cs, Tl$. The concentration and composition dependences of the velocity and attenuation of longitudinal and transversal acoustic waves have been measured, as well as those of the Raman "boson" peak.

The composition and concentration dependence of the acoustic velocity seems to result from two competitive effects : the first one is related to the transition of boron atoms from three- to four coordination with increasing x and the second one to the structural changes connected to the sterical hinderance of the M^+ cations. The maximum frequency of the boson peak has a behaviour similar to that of sound velocity. This similarity can be understood on the basis of the continuum theory of low-frequency Raman spectrum.

Introduction. - The binary borate glasses $B_2O_3 - xM_2O$ are currently used as vitreous matrices for the elaboration of ionic conductors. In order to understand the conduction mechanisms in ternary systems (e.g. $B_2O_3 - xLi_2O - yLiCl$ or $B_2O_3 - xLi_2O - yLi_2SO_4$) (1,2,3), it is necessary in a first step, to get structural informations on the binary matrix. For this purpose we have used the Brillouin and Raman scattering techniques. The identification of the structural units of the glass can be made qualitatively from the analysis of the "high frequency" part of the Raman spectra, while Brillouin experiments can give connection between the acoustical and structural properties. Brillouin results are also of first interest for the interpretation of the so-called Boson peak which dominates the low frequency part of the Raman spectra. Following the Martin and Brenig model (4) the structural correlation range, which reflects the average size of the boron oxygen edifices, can be deduced.

High frequency Raman data. - The amorphous $B_2O_3 - xM_2O$ systems have already been widely studied by Raman spectroscopy (1,5,6). This spectrum is dominated by two lines at 806 cm^{-1} and $780-765\text{ cm}^{-1}$ respectively due to the breathing vibration of boroxol and of six-membered rings containing BO_4 units (di tri tetraborate groups). By a systematic study of all alkali borate glasses (and also Tl_2O containing glasses) we have found different laws for the progressive disappearance of the boroxol 806 cm^{-1} line with increasing values of x : the larger the ionic radius of M^+ , the earlier the 806 cm^{-1} line disappears. This is compatible with an

increase of the dimensions of the borate edifices with increasing sizes of M^+ and can be interpreted from stoichiometric reasons by the dominant formation of triborate groups in the case of $B_2O_3 - x Li_2O$, and tetraborate groups for $B_2O_3 - x Cs_2O$ ($0 < x < 0.3$).

Acoustical results. - The composition and concentration dependencies of the acoustic velocities (v_l and v_t) can be related to these structural changes. In the case of $B_2O_3 - x Li_2O$ glasses, the variation of the velocity reflects essentially the transition of boron-atoms for 3 to 4 coordination with increasing x . As a matter of fact, the curve $v_l = f(x)$ (figure 1) exhibits a similar behaviour as the proportion of B_3 atoms determined by the NMR technique (7). Hence, this transformation ($B_3 \rightarrow B_4$) has a strong tendency to increase the rigidity of the glassy network.

As the mass of the M atom is increased, this coordinance change, which is still present in the glass, has less and less influence on the velocity (figure 1) related to the sterical hinderance of heavy atoms which produces distortions of the glassy network and results in a tendency to reduce its rigidity.

On the other hand, these structural changes have little influence on the attenuation of acoustical waves : this effect appears not to be correlated with local arrangements of atoms but rather to anharmonic processes.

Low-frequency Raman date :
the boson peak. - Figure 2 represents the so-called boson peak observed in a series of borate glasses. The shape and position strongly depend on x and on M .

The scattered Raman intensity (Stokes) is described by the well-known expression (8) :

$$I(\omega) = \frac{1}{\omega} \left(n(\omega) + 1 \right) \cdot C(\omega) \cdot G(\omega)$$

where $n(\omega)$ is the Bose-Einstein population factor. The vibrational density of state $G(\omega)$ has been approximated in the low frequency part by a Debye-like dependency ($G(\omega) \sim \omega^2$). The Martin and Brenig theory (4) has been used for the description of the coupling constant $C(\omega)$. In the framework of this theory, the knowledge of the velocity v_t and v_l allows a determination of the structural correlation range (2σ) from a computer fitting with experimental data (figure 2). The values 2σ obtained with all borate glasses (figure 3) are consistent with the interpretation of the high frequency part of the Raman spectra. In particular for $B_2O_3 - x Li_2O$, (with $x > 0.2$) 2σ does not exceed the dimension of one six-membered ring (this is for instance the case of triborate groups). As the mass of the M atom increases, 2σ also increases ; this agrees with the formation of borate groups containing more than one six-membered rings.

A detailed analysis of these results will be published in a subsequent forthcoming paper.

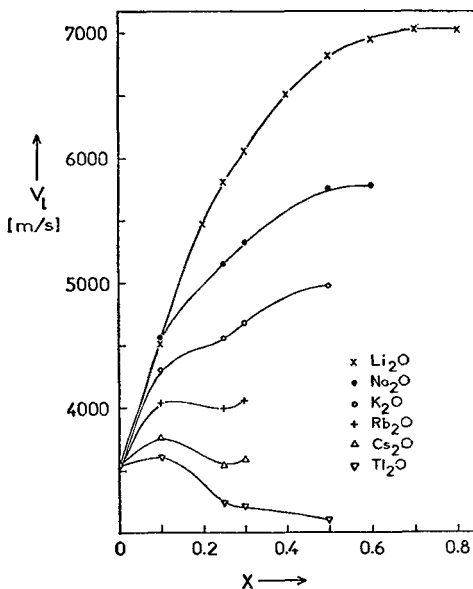


Fig.1 - Velocity of longitudinal acoustic waves versus x and M .

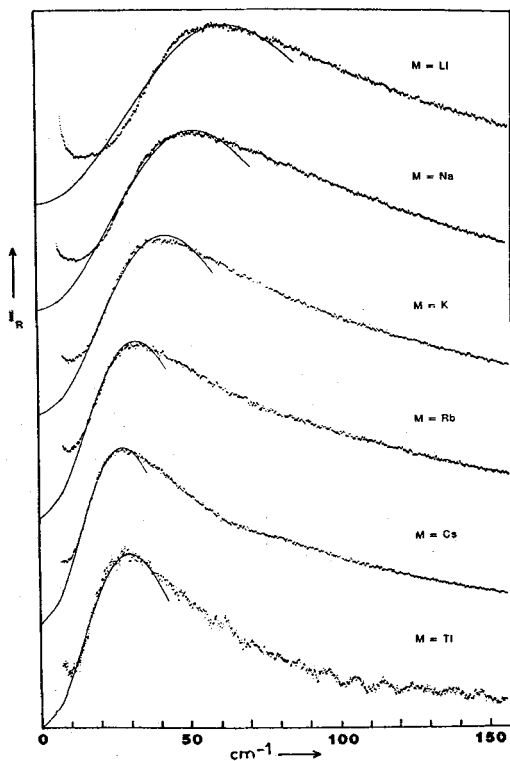


Fig.2 - Low frequency Raman spectra of $B_2O_3 - 0,25 M_2O$ glasses
 — theoretical fits with Martin-Brenig model.

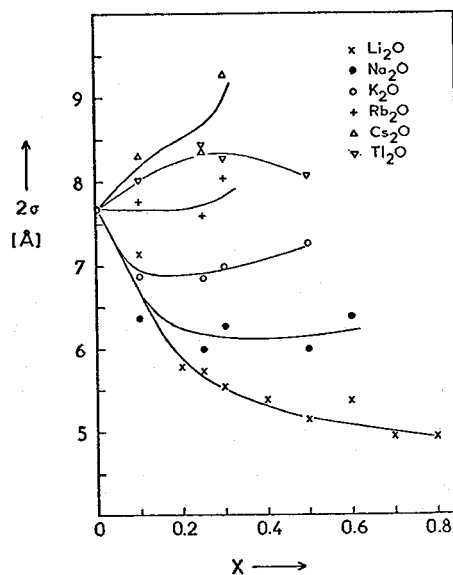


Fig.3 - Structural correlation range deduced from the Martin-Brenig model.

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