

Behavior of density of vibrational states in glassy systems

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The shape of the frequency distribution of the density of vibrational states has been observed, for the first time, to depend on the composition of the glass within a single glassy system.

Various types of behavior of the density of vibrational states in glasses have recently been reported. Neutron-scattering experiments and measurements of the specific heat of glassy SiO_2 have revealed a number of vibrational states in the region 0.3–4 THz in excess of that predicted by the Debye law.¹ In contrast, it was found by Raman scattering in Ref. 2 that the Debye law, $g(w) \sim w^2$, does hold for the density of vibrational states in chalcogenide glasses in the same energy range. It was concluded in Ref. 3 on the basis of similar experiments that there exists a universal behavior of this density of states for all glassy systems, regardless of their chemical composition.

A theoretical expression for the intensity distribution $I(w)$ of Raman scattering in amorphous systems was derived in Ref. 4. For the Stokes part of the spectrum that expression yields $C(w)g(w) = I(w)/\{w\{n(w) + 1\}\}$, where $C(w)$ is the square of the matrix element of the interaction of the exciting photon with the vibrational states, $g(w)$ is the density of vibrational states, and $n(w)$ is a Bose-Einstein distribution function. It was concluded in Ref. 5 on the basis of a study of glassy B_2O_3 at various temperatures that the relation $C(w) \sim w$ holds. The same result was found in Ref. 6, for different glasses, in the region 0.5–2.4 THz, while the relation $C(w) \sim w^2$ was found at lower frequencies. It thus becomes possible to find $g(w)$ from experiments on Raman scattering.

We have studied the low-frequency Raman-scattering spectra of glasses of the composition $(\text{B}_2\text{O}_3)_{0.7}(\text{Cs}_2\text{O})_x(\text{Li}_2\text{O})_{0.3-x}$, where x is in mole percent. This system is interesting because, at a fixed mole composition, there is a continuous replacement of ions of one size and mass, Li^+ , by ions of larger size and mass, Cs^+ . The measurements were carried out at 293 K by the standard procedure in a 90° geometry. Figure 1 shows reduced intensities of the depolarized Raman scattering spectra. In the frequen-

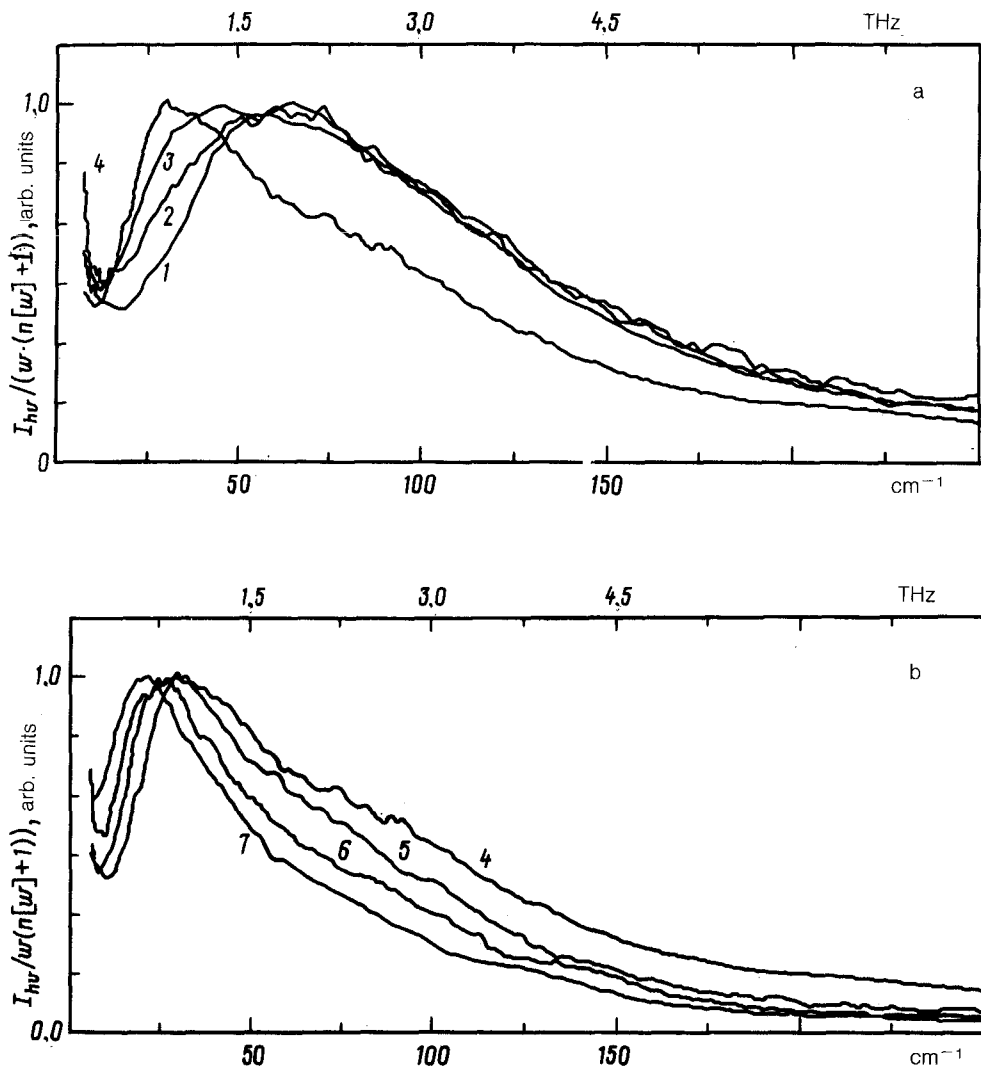


FIG. 1. a: Low-frequency depolarized vibrational spectra of the $(\text{B}_2\text{O}_3)_{0.7}(\text{Cs}_2\text{O})_x(\text{Li}_2\text{O})_{0.3-x}$ glassy system, where x is in mole percent. 1— $x = 0$; 2—0.02; 3—0.04, 4—0.08. b: 4— $x = 0.08$; 5—0.15; 6—0.22; 7—0.30.

cy range $15\text{--}70\text{ cm}^{-1}$ the depolarization coefficient I_{hv}/I_{hh} is 0.48 ± 0.03 for all the glasses. A characteristic feature of these spectra is that the position of the peak and the shape of the band change with the relative concentrations of the alkali ions. Analysis of the band shapes shows that the bands in single-alkali glasses are identical in shape. For glasses with $x \leq 0.05$ we see from Fig. 1a that the curves coincide in the frequency region $60\text{--}150\text{ cm}^{-1}$, while in the region $15\text{--}50\text{ cm}^{-1}$ a component appears and intensifies with increasing x . For glasses with $x \geq 0.06$ this component becomes predominant in shaping the maximum of the entire band, but the component in the region

60–150 cm^{-1} survives; its intensity decreases as $x \rightarrow 0.3$ (Fig. 1b). It follows that the density of vibrational states in a three-component system depends on the relative concentrations of the alkali ions. We observed corresponding results for the Rb–Li cation pair.

In these glasses, the alkali cations are positioned in voids of a framework of boron–oxygen (B–O) structural units: triply and quadruply coordinated B atoms near bridge and nonbridge oxygen atoms (NBOs).^{7,8} The Cs^+ ion may be part of larger B–O groupings, since its volume is roughly 14 times that of Li^+ . The larger Cs^+ alkali ions have a tendency to disrupt the B–O network, increasing the number of NBOs and creating a neighborhood which is packed considerably less densely than that of the Li^+ ions. Noting that the alkali cations are distributed in a random fashion at low concentrations of one of the ions, the three-component system can be represented as consisting of two types of structural groupings, which contain the corresponding alkali ion. Structural groupings of this sort have been identified for single-alkali systems near certain modifier concentrations.^{7,8} Each determines a corresponding component of the density of vibrational states, so it might be suggested that the spectral shape of the Raman scattering would be additive for a three-component system. An effort was accordingly undertaken to resolve the experimental spectrum into components corresponding to single-alkali systems (Fig. 2). The component which remained after the subtraction of the “lithium” spectrum has a shape similar to that of the Raman-scattering band in a single-alkali system. The position of its peak and the value of its half-width are equal to the corresponding values in the spectrum for the single-alkali cesium borate glass. A decomposition of this sort is possible at small values $0.01 \leq x < 0.06$. In the region of equal concentrations of the alkali cations, we know that a polyalkali effect occurs (a decrease in the ion mobility). This effect stems from the appearance of structural groupings which are not found in single-alkali systems and which are caused⁹ by the interaction of unlike alkali ions. One might suggest that such

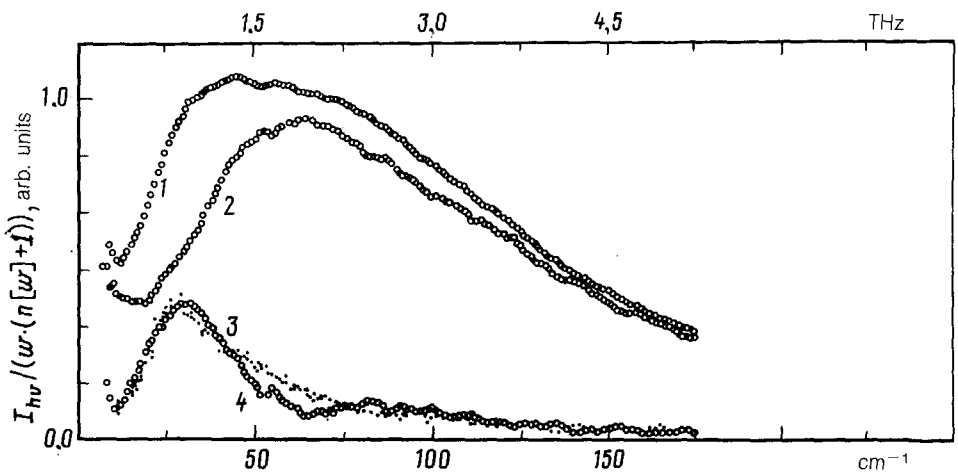


FIG. 2. Decomposition of the vibrational spectrum of a three-component glass into components corresponding to single-alkali glasses. 1— $x = 0.04$; 2— $x = 0.4$; 4—the difference (1–2); 3— $(\text{Cs}_2\text{O})_{0.04} \cdot (\text{B}_2\text{O}_3)_{0.96}$.

structural groupings also contribute to the vibrational states, along with the structural groupings characteristic of single-alkali systems. The resolution of the spectrum into components is therefore ambiguous in the region $x \approx 0.15$. In the case $x \rightarrow 0.3$ it becomes necessary to also consider the contribution of the Cs-O vibration with a peak near 100 cm^{-1} (Ref. 10).

These results show that the density of vibrational states in two-alkali borate glasses is determined by the relative concentrations of the alkali cations, and it reflects the existence of different types of structural groupings. At low concentrations of one of the cations, this density of states is an additive function of the density of vibrational states of single-alkali systems.

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¹U. Buchenau *et al.*, Phys. Rev. B **57**, 757 (1986).

²R. J. Nemanich, J. Non-Cryst. Solids **59-60**, 851 (1983).

³M. G. Zemlyanov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **49**, 521 (1989) [JETP Lett. **49**, 602 (1989)].

⁴R. Shuker and R. W. Gammon, Phys. Rev. Lett. **25**, 222 (1970).

⁵S. Guha and G. E. Walrafen, J. Chem. Phys. **80**, 3807 (1984).

⁶V. K. Malinovsky *et al.*, Europhys. Lett. **11**, 43 (1990).

⁷J. Lorösch *et al.*, J. Non-Cryst. Solids **69**, 1 (1984).

⁸W. J. Soppe *et al.*, J. Non-Cryst. Solids **93**, 142 (1987).

⁹W. J. Soppe *et al.*, J. Non-Cryst. Solids **104**, 22 (1988).

¹⁰G. J. Exarhos and W. M. Risen, Jr., Solid State Commun. **11**, 755 (1972).

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