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ELECTROSTRICTION EFFECT IN GLASS

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The longitudinal electrostriction tensor component Q_{11} in polarization notation and M_{11} in electric field notation for sodium trisilicate glass and sodium aluminosilicate glass has been measured by the converse method, i.e. by measuring the slope of the uniaxial stress dependence of the dielectric constant at various frequencies. For sodium trisilicate glass, the Q_{11} coefficient strongly depends on the frequency at which the capacitance was measured and shows a maximum near the frequency of 150 Hz, which is the ionic relaxation frequency of the glass. For sodium aluminosilicate glass, the relative change in the dielectric constant in response to a uniaxial stress was, however, found to be much smaller. We construct a sodium ion hopping model to explain qualitatively the results.

1. Introduction

The quadratic electrostriction effect is the basic electromechanical coupling effect in centric crystals and isotropic glasses. There are two alternative experimental approaches to the measurement of electrostriction; the direct method, which is to measure directly the elastic strain induced by a high electrical field and the converse method, in which the thermodynamically equivalent change in dielectric stiffness under mechanical stress is measured. Both methods are very difficult. In the direct method, the electrostrictive strain levels which can be induced at a realizable high electric field on low-permittivity centric crystals are only of the order of 10^{-10}. So that an ultradilatometer or interferometer of the sensitivity of 10^{-13} m is the only possible instrument to measure the minute strain. For the converse method, the need for high sensitivity is transferred to the dielectric measurement. Modern measuring systems like the General Radio 1620 capacitance bridge do have the sensitivity and stability required, but there is now also need for very precise temperature control and the establishment of a truly uniaxial stress upon the sample.

So far, hydrostatic electrostriction coefficients have been measured for several insulator crystals with simple centric structures, but except for high-permittivity perovskite structure oxides, reliable values of the separated tensor components of electrostriction are rare in the literature [1]. In the case of the simple alkali halides, even the signs of the coefficients are in doubt [2,3] and there is considerable uncertainty as to the influence of the defect structure upon the measured values [4].

Glass is interesting because of the amorphous structure and metastability. We can picture the silica glass, from Zachariasen, to be a random but continuous, network of $(SiO_3)^{2-}$ tetrahedra. Thermodynamically, the glass state is metastable, i.e. there is always a crystalline assembly with a lower Gibbs free energy. The measurement of the longitudinal electrostriction coefficient of glass is of interest, because taken in conjunction with hydrostatic measurements, the complete electrostriction tensor can be defined.

It has been suggested that electrostriction is responsible for the unusual effects of electric field upon crack propagation in glass samples, but heretofore, reliable experimental electrostriction data on representative glasses have not been available.

In this work, the converse method for the electrostriction measurement was performed on sodium trisilicate glass and sodium aluminosilicate glass. The two glasses are chosen as the samples for this study because the ionic relaxation frequency of these glasses are close to 150 Hz at room temperature, within the range of the General Radio 1620 capacitance measurement system used for the converse electrostriction measurements.

2. Basic principles

M_{ijkl} and Q_{ijkl}, the electrostrictive coefficients in electric field and polarization notations, respectively, are defined by the relations:

$$M_{ijkl} = \tfrac{1}{2}\,(\partial^2 x_{ij}/\partial E_k\,\partial E_l)_X\,, \tag{1}$$

$$Q_{ijkl} = \tfrac{1}{2}\,(\partial^2 x_{ij}/\partial P_k\,\partial P_l)_X \tag{2}$$

and by applying Maxwell's relations to eqs. (1) and (2),

$$M_{ijkl} = \tfrac{1}{2}\,(\partial \delta_{kl}/\partial X_{ij})_P\,, \tag{3}$$

$$Q_{ijkl} = -\tfrac{1}{2}\,(\partial \chi_{kl}/\partial X_{ij})_P\,, \tag{4}$$

where χ_{kl} and δ_{kl} are the components of the dielectric stiffness and dielectric susceptibility, respectively. It may be noted for materials of central symmetry that

$$\chi_{kl} = 1/\delta_{kl} = 1/\epsilon_0(\epsilon_{kl} - 1)\,, \tag{5}$$

where ϵ_0 is the permittivity of free space and ϵ_{kl} the components of the relative permittivity tensor. Thus

$$M_{ijkl} = \tfrac{1}{2}\,\epsilon_0\,(\partial \epsilon_{kl}/\partial X_{ij})_P\,, \tag{6}$$

$$Q_{ijkl} = [\epsilon_0(\epsilon_{kl} - 1)]^{-2} M_{ijkl}\,, \tag{7}$$

$$= [2\epsilon_0(\epsilon_{kl} - 1)^2]^{-1}\,(\partial \epsilon_{kl}/\partial X_{ij})_P\,. \tag{8}$$

We used a thin circular disk of the specimen for the converse method of measurement. So the capacitance is given by

$$C = \epsilon_0 \epsilon A/d\,. \tag{9}$$

The change of permittivity under the mechanical stress is related to the change in the capacitance and the geometry change under stress:

$$\partial\epsilon/\partial X = \epsilon(C^{-1}\,\partial C/\partial X - S)\,, \tag{10}$$

where S is the appropriate combination of the components of the compliance tensor.

Glass is isotropic, so its dielectric constant tensor and fourth-rank tensor in Voigt notation have the form:

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \epsilon & 0 & 0 \\ 0 & \epsilon & 0 \\ 0 & 0 & \epsilon \end{pmatrix}, \tag{11}$$

$$\mathbf{M} = \begin{pmatrix} M_{11} & M_{12} & M_{12} & 0 & 0 & 0 \\ M_{12} & M_{11} & M_{12} & 0 & 0 & 0 \\ M_{12} & M_{12} & M_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & M_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & M_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & M_{44} \end{pmatrix}, \tag{12}$$

where

$$M_{44} = 4M_{1212} = 4 \times \tfrac{1}{2}(M_{11} - M_{12}) = 2(M_{11} - M_{12})\,. \tag{13}$$

For the longitudinal electrostriction effect, S in eq. (10) is

$$S = -(s^{\mathrm{T}}_{11} - 2s^{\mathrm{T}}_{12}) = ((1)/(9K)) - ((2)/(3\mu))$$

$$= ((1)/(E)) - ((1)/(\mu)) \tag{14}$$

where s^{T}_{ij} is the component of the compliance tensor in Voigt notation, K and μ are the bulk and shear elastic moduli, respectively [5].

3. Experimental procedures

The elastic data and dielectric data for sodium trisilicate glass can be found in refs. [6,7].

We measured the sodium aluminosilicate glass. The elastic data can be obtained by the measurement of the density and the longitudinal and transverse sound speeds in the ultrasonic wave pulse superposition technique. The specimen of thickness 1.393 cm was measured at 20 MHz with an accuracy of one part in 10^4. The elastic data are summarized in table 1. For the dielectric measurement of sodium aluminosilicate glass, we used a sample in the form

Table 1
Density, sound speeds, and elastic data of the sodium trisilicate glass and sodium aluminosilicate glass

Material	ρ (kg/dm^3)	C_l (m/s)	C_t (m/s)	E (10^8 N/m^2)	K (10^8 N/m^2)	μ (10^8 N/m^2)	σ
$Na_2O \cdot 3SiO_2$ [a]	–	5374	3222	614	365	252	0.219
sodium aluminosilicate	2.42	5529	3329	653	383	269	0.216

[a] Data taken from ref. [6].

of a circular plate 23 mm across and 1.5 mm thick. We evaporated aluminum electrodes on the two planes of less than 1 μm roughness, with a guard gap 0.1 mm wide and 16 mm across made on the "low" electrode.

The dielectric constant and dielectric loss of the glass was measured from 0.1 Hz to 10 MHz. 10 kHz to 10 MHz was covered using a Hewlett–Packard 4274A multi-frequency LCR meter and 100 Hz to 100 kHz using a Hewlett–Packard 4275A multi-frequency LCR meter.

The frequency range of 0.1 Hz to 100 Hz was covered by a Sawyer–Tower circuit with added compensation circuit. We adjust to a horizontal line in the oscilloscope display of D and E when the capacitance and conductance is exactly matched by the parallel combination of a real capacitor and resistor. Such measurement can give a good resolution of 1 pF and 1 MΩ in capacitance and resistance, respectively.

K', K'' and σ (the effective conductivity) as functions of frequency for sodium aluminosilicate glass at room temperature (22°C) are plotted in fig. 1. At low frequencies K' is expected to level off at a value K_0. But the electrode polarization effect becomes dominant with decreasing frequency starting

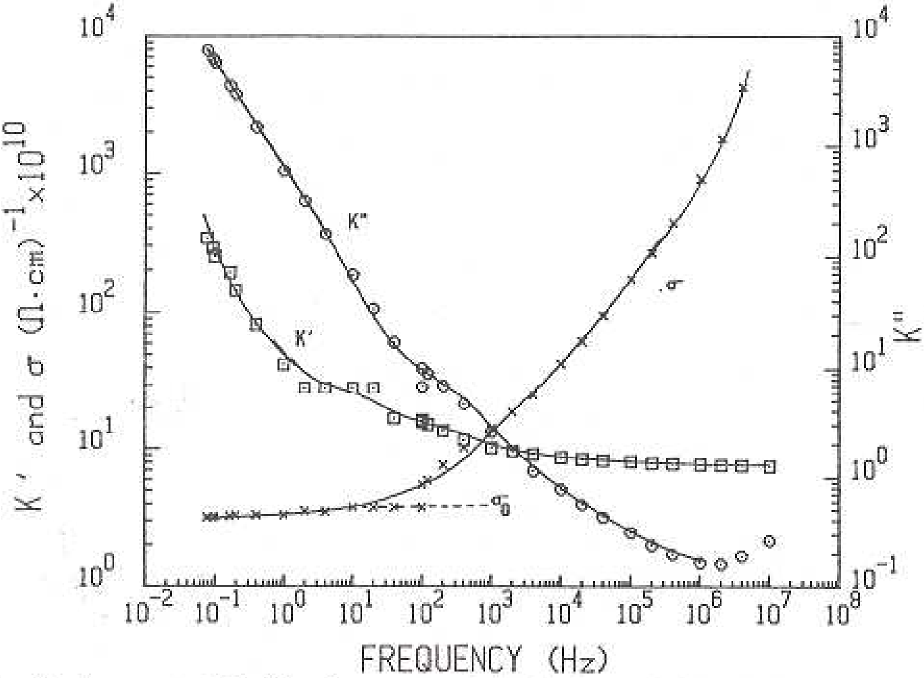

Fig. 1. The real and imaginary parts of the dielectric constants and the effective conductivity of the sodium aluminosilicate glass as a function of frequency.

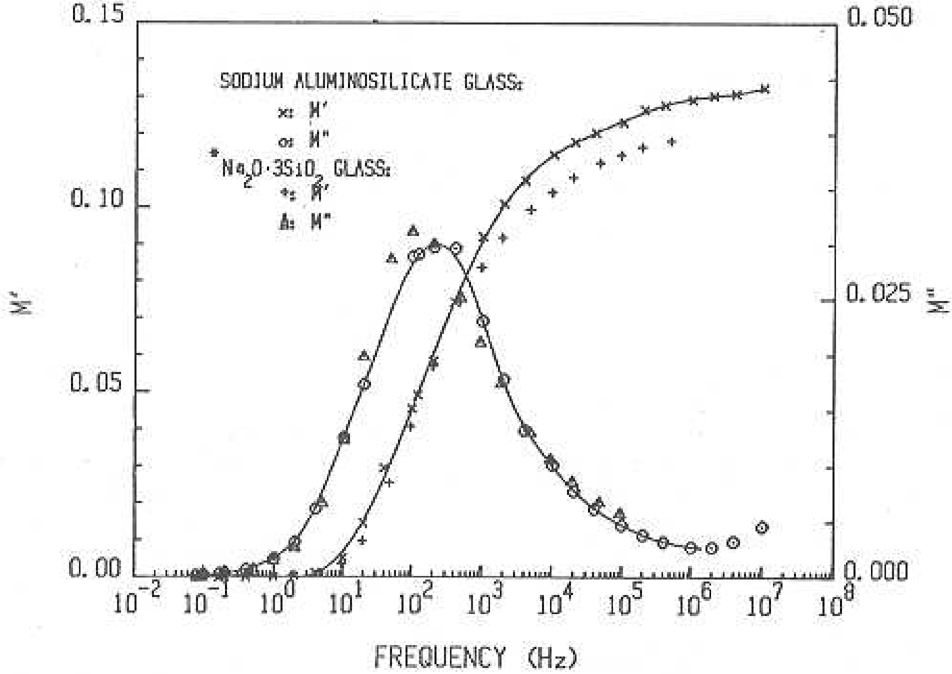

Fig. 2. The real and imaginary parts of the inverse dielectric constants of the sodium aluminosilicate glass and $Na_2O \cdot 3SiO_2$ glass. *: data taken from ref. [6].

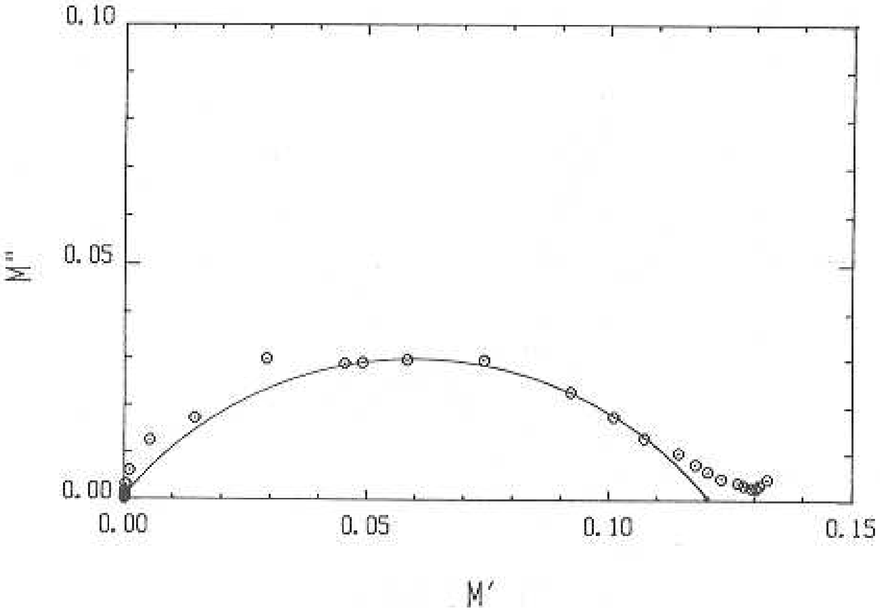

Fig. 3. Cole–Cole plot of the complex inverse dielectric constant of the sodium aluminosilicate glass.

from ≈20 Hz. We can eliminate the electrode polarization effect by using the regime of the complex inverse dielectric constant or electrical modulus, M^*, which is defined as

$$\begin{aligned} M^* &= 1/K^* = 1/(K' - \mathrm{i}K'') \\ &= K'/[(K')^2 + (K'')^2] + K''/[(K')^2 + (K'')^2] \\ &= M' + M'' . \end{aligned} \tag{15}$$

M' and M'' as functions of frequency are shown in fig. 2. They just show relaxation spectra. The M'' curve exhibits a clear peak near 150 Hz, which is the so-called relaxation frequency. The plot of M'' is asymmetric with respect to the peak maximum, and is considerably broader on both sides of the maximum than would be for a single dipole relaxation time. A Cole–Cole plot of M' and M'' is shown in fig. 3.

The dc compressometer designed and built by Meng and Cross [1] was used for the converse method of electrostriction measurement. The capacitance decreases in response to the uniaxial stress in sodium trisilicate glass and sodium aluminosilicate glass. The $Na_2O{\cdot}3SiO_2$ glass was measured at 10 V, various frequencies (fig. 4); the sodium aluminosilicate glass at 10 V, 100 Hz; 30 V, 100 Hz (fig. 5). The data for vitreous silica glass for hydrostatic pressure were obtained by taking the slope $-\epsilon^{-1}(\partial\epsilon/\partial P)_T$ from Reitzel [8].

All data are summarized in table 2.

4. Discussion

We see from table 2 that though sodium trisilicate glass and sodium aluminosilicate glass respond dielectrically to ac electric field in a quite similar manner, they respond to uniaxial stress rather differently. $C^{-1}\,\partial C/\partial X$ is large in sodium trisilicate and the Q_{11} of the glass strongly depends on the frequency at which the capacitance was measured (fig. 6). $C^{-1}\,\partial C/\partial X$ of sodium aluminosilicate glass was, however, found to be smaller and the Q_{11} of sodium aluminosilicate glass does not change so much with frequency. We believe that the difference between the sodium trisilicate

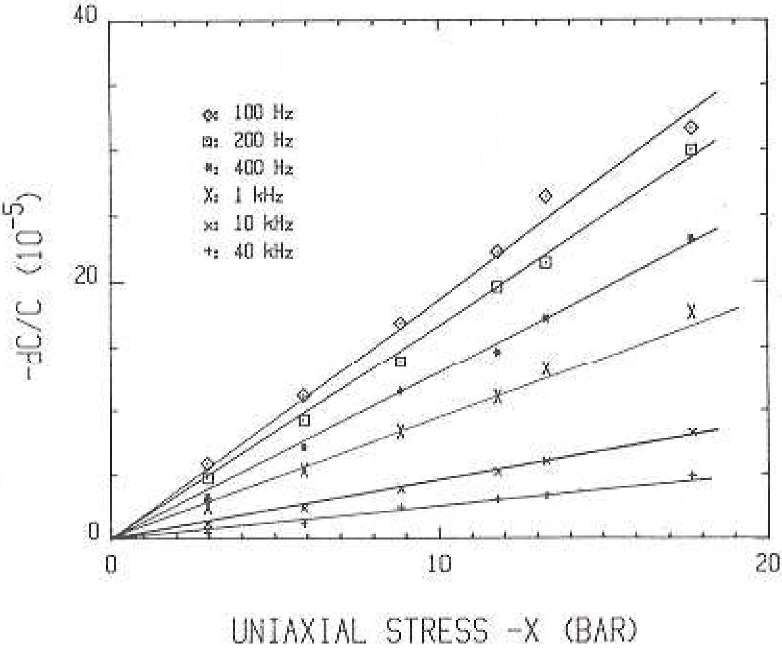

Fig. 4. Uniaxial stress dependence of the relative change of capacitance of $Na_2O{\cdot}3SiO_2$ glass.

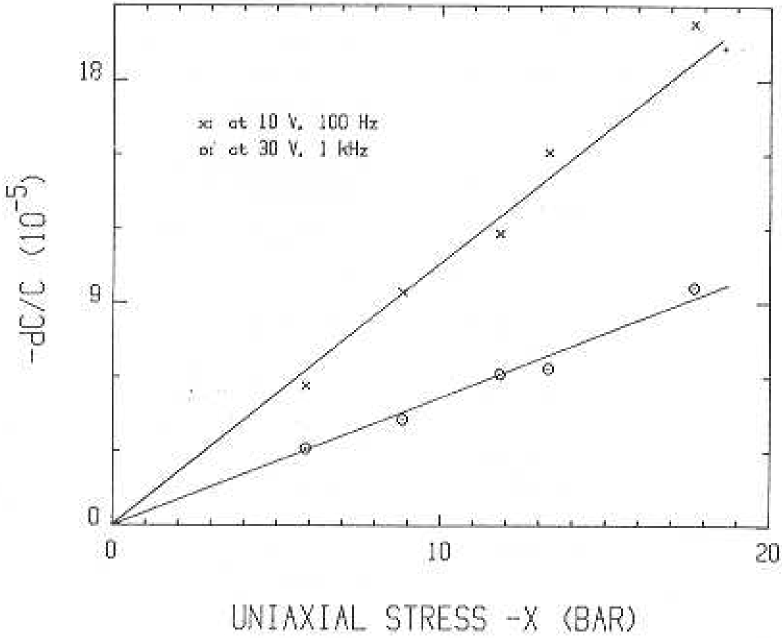

Fig. 5. Uniaxial stress dependence of the relative change of capacitance of the sodium aluminosilicate glass.

Table 2
Electrostrictive coefficients for silica glasses and quartz

Material	f (Hz)	K	$C^{-1}\partial C/\partial X$ (10^{-11} Pa^{-1})	M_{11} (10^{-20} m^2 V^{-2})	Q_{11} (m^4 C^{-2})	
$Na_2O \cdot 3SiO_2$	10^2	15.5	18.1	1.40	0.851	
	2×10^2	13.8	17.1	1.19	0.923	
	4×10^2	12.13	13.5	0.849	0.874	
	10^3	11.3	10.3	0.631	0.765	
	10^4	9.36	4.82	0.297	0.541	
	4×10^4	8.82	2.95	0.207	0.430	
sodium aluminosilicate	10^2	15.7	12.4	1.01	0.599	
	10^3	10.2	5.45	0.346	0.519	
X-cut quartz	–	4.34 (⊥ c axis)	–	−0.06 ± 0.02 a)	−0.69 ± 0.23	
	f (Hz)	K	$-\epsilon^{-1}\partial\epsilon/\partial p$ (10^{-11} Pa^{-1})	M_h (10^{-20} m^2 V^{-2})	Q_h (m^4 C^{-2})	T (°C)
vitreous silica	2.5×10^3	3.8	1.62 b)	0.0272	0.443	20
	2.5×10^3	3.8	1.35 b)	0.0227	0.370	138

a) Data taken from ref. [9] using the direct method.
b) Data read from ref. [8].

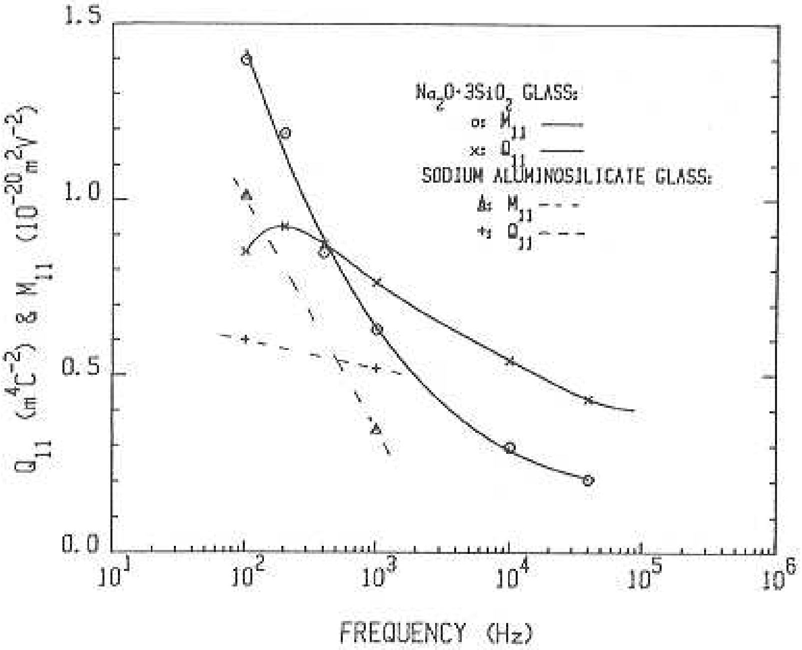

Fig. 6. Longitudinal electrostrictive coefficients of $Na_2O \cdot 3SiO_2$ glass and the sodium aluminosilicate glass as a function of frequency.

and the sodium aluminosilicate may be accounted for qualitatively in the following manner.

In the sodium silicate glass, the extra oxygen introduced by the Na_2O is non-bridging in the silicate structure. The addition of alumina reduces the number of these non-bridging oxygens so that at the Al/Na = 1 ratio all have been eliminated. Earlier literature on the conduction [10] shows that the activation energy for conduction decreases with the reduction in non-bridging oxygen content and is a minimum at the Al/Na = 1 ratio. In these papers, the effect is attributed to the expansion of the coordination shell in the silicate framework about the Na^+ ion, with the reduction in non-bridging oxygen content.

It was proposed that this change in volume of the coordination shell could be electrostatic in origin, or could be due to the modification in the adjustment of orbitals interacting with the sodium ion between bridging and non-bridging oxygens.

Whatever the origin, it is clear that if the Na^+ ion is in an expanded cage, hopping of the Na^+ ion may be accomplished with less effect on the geometry of the cage structure so that in the aluminosilicate the Na polarizability contributes less strongly to electrostriction.

When the sodium ions become immobilized at very high frequency, the electrostriction reponse must be largely that of the unmodified network, and it is interesting to note that in vitreous silica $Q_h \approx 0.443$ m^4 C^{-2}, rather close to the highest frequency value of Q_{11} for the trisilicate glass.

Since there is in these measurements a rather clear evidence of the role of the network modifier in changing the electrostrictive response, it will be most interesting to explore the role of alternative but very different network modifiers such as boron, and these studies are now underway.

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