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DIELECTRIC LOSSES OF ALKALI METAPHOSPHATE GLASSES IN THE LOW TEMPERATURE RANGE 4–200 K, AND THEIR RELATION TO THE GLASS COMPOSITION

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Dielectric losses of Li, Na, K, Rb and Cs metaphosphate glasses have been studied in the temperature range 4–200 K. In the sodium containing glasses the ratio of linear to cyclic phosphates was varied by adding cyclic tri or tetrametaphosphate. The height of the loss peak, $\tan\delta$ (max), increases with an increasing amount of cyclic metaphosphates in the glass.

1. Introduction

Dielectric losses have been studied extensively in silicate, borate and phosphate glasses in the temperature range 200–700 K [1]. Dielectric losses of borate glasses in the low temperature range, 4–200 K, were studied by van Gemert and Stevels [2,3] in our institute. It seemed appropriate to extend their investigations to phosphate glasses.

Mainly through the work of Westman [4], it is known that alkali metaphosphate glasses contain linear as well as cyclic metaphosphate molecules in greatly varying amounts. Upon changing the ratio of the number of cyclic molecules to the number of linear molecules, a change in the mobility of the glass network is expected, and, consequently, a correlation between this ratio and the dielectric losses of the glasses. A fortunate circumstance is that a quantitative analysis of phosphate glasses is not too difficult since the latter may be dissolved in water without significantly changing their composition.

2. Experimental

Alkali (Li, Na, K, Rb and Cs) metaphosphate was made by heating a mixture of alkali carbonate (Merck) and ammonium mono-hydrogen ortho-

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phosphate with a molar ratio 1 : 2 in a platinum crucible in an electric furnace at 900°C. After three hours, no further weight loss occurred and the molar ratio alkali to phosphor remained equal to one. The melt was poured out onto a steel plate and immediately flattened with a cold flat-iron into a sheet, approximately 2 mm thick.

In order to obtain a series of phosphate glasses with a varying cyclic to linear ratio but containing the same alkali metal, varying amounts of cyclic sodium trimetaphosphate (Ventron), cyclic sodium tetrametaphosphate (prepared according to Brauer [5] and Pascal [6]), sodium orthophosphate (Merck), and sodium pyrophosphate (Merck, respectively, were added to sodium metaphosphate at 900°C in the furnace. After these additions the melts were held for two minutes in the furnace, and then processed as described above.

Cylindrical samples of 25 mm diameter were machined out of the glass sheets, ground to a thickness of 1 to 2 mm, and polished. The samples were mounted between blocking electrodes in a cryostat which was specially designed by Oxford Instruments Co., and is described in ref. 3. The samples between the electrodes were a part of a Wheatstone's bridge, equipped with a Rhode and Schwarz RC generator (Type SRM BN 4085), a dielectric test bridge (Type VRB BN 12 121/2), and a tunable indicator amplifier (Type VRB BN 3520). The loss measurements were carried out between 5 and 200 K at frequencies ranging from 0.1 to 100 kHz.

In order to determine the amounts of the various components in the phosphate glasses (cyclic tri and tetrametaphosphate, and orthophosphate) we followed the chromatographic method of Crowther [7]. However, instead of paper, we used Merck 20×20 cm plates covered with cellulose F. In the elution liquid we used trichloro-acetic instead of formic acid. We did not analyse for cyclic penta- and higher phosphates, since it is known from the work of Westman that these are only present in small amounts.

3. Results and discussion

The results of our measurements on the sodium glasses are shown in figs. 1 and 2.

It can be seen from these figures that the curve for tan δ versus temperature is a superposition of the tail of the loss curve which is due to the migration of the alkali ions (having its maximum far above 200 K), and of the loss curve for a process which causes dielectric losses to occur in the low temperature region. Stainless steel blocking electrodes were used to separate the two loss peaks as far as possible. We assume that the contribution of the migration peak to the low-temperature losses becomes negligible below 140 K for the Li and Na glasses, and below 200 K for the K, Rb and Cs glasses, and that the tail of the alkali migration peak has an exponential shape [8,9]. We may then fit an

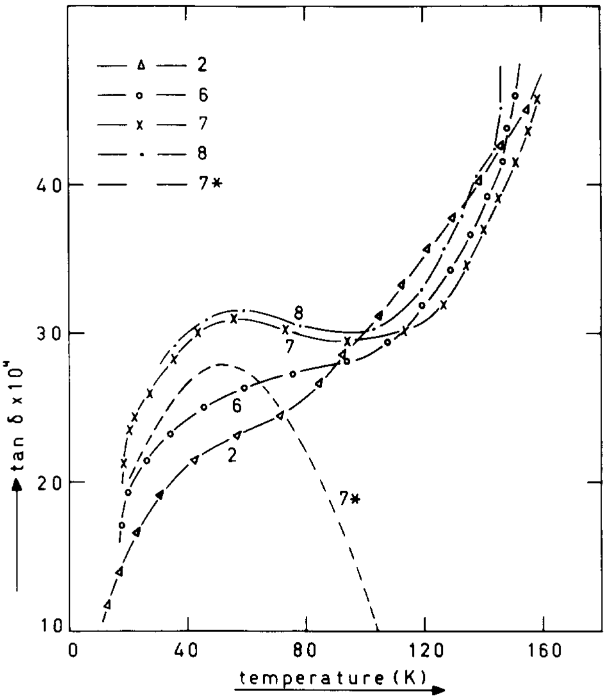

Fig. 1. Dielectric loss curves for sodium phosphate glasses. Sample 2, $Na_2OP_2O_5$; samples 6, 7 and the same 8 with the addition of cyclic trimetaphosphate (cf. tables 1 and 2). Curve 7* shows the peak of sample 7 after the subtraction of the exponential background due to the migration loss peak.

Table 1

Overall composition, analyzed cyclic metaphosphate contents, and tan δ (max) at 1 kHz for a series of alkali metaphosphate glasses. The concentrations of the cyclic phosphates were determined from five observations, standard deviation ≈ 0.6, except for sample 5 where it was as large as 2.5. The orthophosphate concentration was less than 1 mol.% in all cases

Sample No.	Overall composition	Cyclic trimeta-phosphate (mol.%)	Cyclic tetrameta-phosphate (mol.%)	Total cyclic Metaphosphate (mol.%)	tan δ (max) $\times 10^4$ (at 1 kHz)
1	$Li_2OP_2O_5$	11.5	7.6	19.1	20.0
2	$Na_2OP_2O_5$	12.2	12.5	24.7	20.0
3	$K_2OP_2O_5$	14.4	20.3	34.7	36.4
4	$Rb_2OP_2O_5$	10.6	< 1	10.6	16.4
5	$Cs_2OP_2O_5$	6.2	< 1	6.2	16.4
	$Na_2OP_2O_5$ with addition of:				
6	5 mol.% cyclic trimetaphosphate	17.0	12.6	29.6	22.0
7	10 mol.% cyclic trimetaphosphate	22.5	12.8	35.3	28.2
8	15 mol.% cyclic trimetaphosphate	26.9	12.5	39.4	28.5
9	5 mol.% cyclic tetrametaphosphate	12.2	17.9	30.1	21.5
10	10 mol.% cyclic tetrametaphosphate	12.2	22.5	34.7	28.2
11	15 mol.% cyclic tetrametaphosphate	12.7	27.4	40.1	28.4

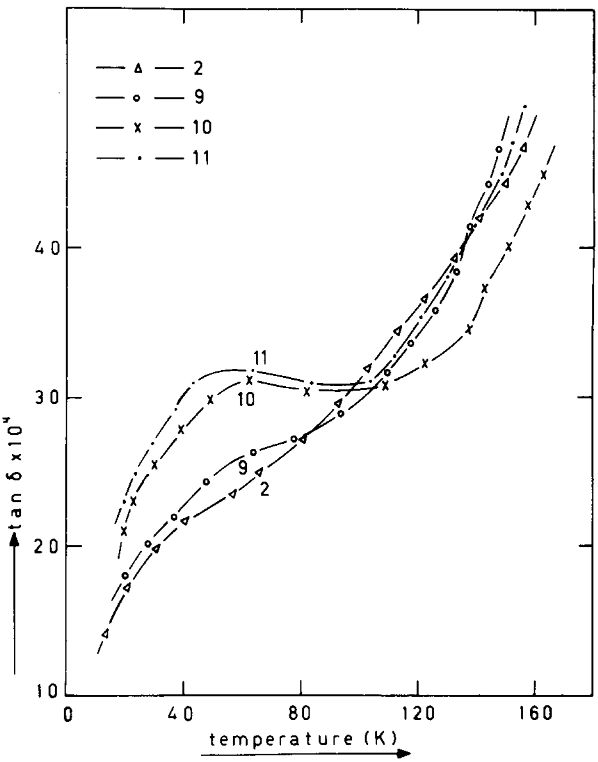

Fig. 2. Dielectric loss curves for sodium phosphate glasses. Sample 2, $Na_2OP_2O_5$; samples 9, 10 and 11 the same with the addition of cyclic tetrametaphosphate (cf. table 1 and 2).

exponential line through the origin and the experimental points above 140 K (or 200 K) and subtract this background from the experimental curve to obtain a line which is due to the low-temperature process only (cf. curve 7* in fig. 1 as an example). Although this a a rather rough procedure, we may determine in this manner the temperature of the maximum in the low-temperature loss

Table 2
Activation energies $Q \pm 0.01$ eV, and temperatures T_{max} at a frequency of 1 kHz of the low-temperature loss peak for alkali metaphosphate glasses

Sample no.	Overall composition	Q(eV)	T_{max} (K)
1	$Li_2OP_2O_5$ [a]	0.07; 0.17	43; 81
2	$Na_2OP_2O_5$	0.09	52
3	$K_2OP_2O_5$	0.21	120
4	$Rb_2OP_2O_5$	0.25	120
5	$Cs_2OP_2O_5$	0.21	100
6–11	$Na_2OP_2O_5$ plus cyclic		52–56

[a] For the Li-glasses a splitting into two peaks is observed.

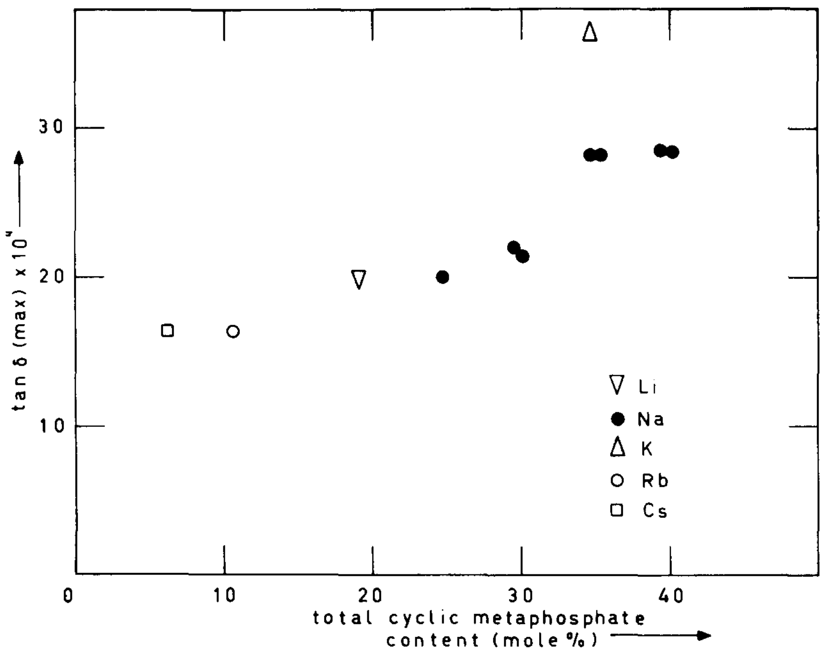

Fig. 3. Plot of tan δ(max) versus the total cyclic metaphosphate content for the low-temperature dielectric loss peaks of the alkali metaphosphates.

curve, T_{max}, and the value for tan δ (max). These maxima are shown in table 1 together with the results of the chemical analysis (for the Li glass two peaks are observed).

It is clear from fig. 3 where tan δ (max) is plotted versus the total cyclic metaphosphate content that the dielectric losses increase with the number of cyclic molecules per mole of metaphosphate glass.

On the other hand, addition of sodium ortho- and pyrophosphate gives no increase in tan δ (max) for the sodium metaphosphate glass.

Though the peaks do not show the Debye shape it may be assumed that the relaxation process is thermally activated and that the Arrhenius equation $\tau = \tau_0 \exp(Q/kT)$ is valid. It is then possible to determine a mean activation energy for the process from the shift of T_{max} as a function of frequency. The resulting Q-values, together with T_{max} at a frequency of 1 kHz, are given in table 2. A typical value $\tau_0 \approx 5 \times 10^{-14}$ s is observed, for the relaxation time, i.e. τ_0^{-1} is of the order of a vibrational frequency. The activation energies of 0.07–0.2 eV strongly suggest a relaxation due to the so-called inherent local motions [3,10].

The observed correlation between tan δ (max) and the amount of cyclic molecules indicates that the process is related to motions in the phosphate rings. This supposition is corroborated by the following calculation. The value of the relaxation strength, at T_{max}, $\Delta\epsilon$ can be estimated from the area under the curve of tan δ versus T^{-1} [3]. From $\Delta\epsilon$, a value of p^2N can be obtained, where

p is an averaged dipole moment and N is the concentration of dipoles. For instance, for sample 3, we find $p^2N \sim 5 \times 10^{20}$ Debye^2 cm^{-3} (45×10^4 C^2 m^{-1}). Assuming that dipoles of the order of a Debye unit are involved, in accordance with experimental results for various glasses [10,11] we obtain $N \sim 10^{20}$ cm^{-3}. This value is well within the range expected for motions of the ring system.

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