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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 phospho-
phate 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 mole-
cules 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$_2$OP$_2$O$_5$; 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 $\approx 0.6$, except for sample 5 where it was as large as 2.5. The
orthophosphate concentration was less than 1 mol.% in all cases.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Overall composition</th>
<th>Cyclic trimetaphosphate (mol.%)</th>
<th>Cyclic tetrametaphosphate (mol.%)</th>
<th>Total cyclic Metaphosphate $\times 10^4$ (at 1 kHz)</th>
<th>tan δ (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li$_2$OP$_2$O$_5$</td>
<td>11.5</td>
<td>7.6</td>
<td>19.1</td>
<td>20.0</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$OP$_2$O$_5$</td>
<td>12.2</td>
<td>12.5</td>
<td>24.7</td>
<td>20.0</td>
</tr>
<tr>
<td>3</td>
<td>K$_2$OP$_2$O$_5$</td>
<td>14.4</td>
<td>20.3</td>
<td>34.7</td>
<td>36.4</td>
</tr>
<tr>
<td>4</td>
<td>Rb$_2$OP$_2$O$_5$</td>
<td>10.6</td>
<td>$&lt;1$</td>
<td>10.6</td>
<td>16.4</td>
</tr>
<tr>
<td>5</td>
<td>Cs$_2$OP$_2$O$_5$</td>
<td>6.2</td>
<td>$&lt;1$</td>
<td>6.2</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>Na$_2$OP$_2$O$_5$ with addition of:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5 mol.% cyclic trimetaphosphate</td>
<td>17.0</td>
<td>12.6</td>
<td>29.6</td>
<td>22.0</td>
</tr>
<tr>
<td>7</td>
<td>10 mol.% cyclic trimetaphosphate</td>
<td>22.5</td>
<td>12.8</td>
<td>35.3</td>
<td>28.2</td>
</tr>
<tr>
<td>8</td>
<td>15 mol.% cyclic trimetaphosphate</td>
<td>26.9</td>
<td>12.5</td>
<td>39.4</td>
<td>28.5</td>
</tr>
<tr>
<td>9</td>
<td>5 mol.% cyclic tetrametaphosphate</td>
<td>12.2</td>
<td>17.9</td>
<td>30.1</td>
<td>21.5</td>
</tr>
<tr>
<td>10</td>
<td>10 mol.% cyclic tetrametaphosphate</td>
<td>12.2</td>
<td>22.5</td>
<td>34.7</td>
<td>28.2</td>
</tr>
<tr>
<td>11</td>
<td>15 mol.% cyclic tetrametaphosphate</td>
<td>12.7</td>
<td>27.4</td>
<td>40.1</td>
<td>28.4</td>
</tr>
</tbody>
</table>
Fig. 2. Dielectric loss curves for sodium phosphate glasses. Sample 2, Na$_2$OP$_2$O$_5$; 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 is 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 $T_{\text{max}}$ at a frequency of 1 kHz of the low-temperature loss peak for alkali metaphosphate glasses

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Overall composition</th>
<th>$Q$(eV)</th>
<th>$T_{\text{max}}$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li$_2$OP$_2$O$_5$, a</td>
<td>0.07; 0.17</td>
<td>43; 81</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$OP$_2$O$_5$</td>
<td>0.09</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>K$_2$OP$_2$O$_5$</td>
<td>0.21</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>Rb$_2$OP$_2$O$_5$</td>
<td>0.25</td>
<td>120</td>
</tr>
<tr>
<td>5</td>
<td>Cs$_2$OP$_2$O$_5$</td>
<td>0.21</td>
<td>100</td>
</tr>
<tr>
<td>6–11</td>
<td>Na$_2$OP$_2$O$_5$ plus cyclic</td>
<td>52–56</td>
<td></td>
</tr>
</tbody>
</table>

* 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, \( T_{\text{max}} \), 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 \( T_{\text{max}} \) as a function of frequency. The resulting \( Q \)-values, together with \( T_{\text{max}} \) at a frequency of 1 kHz, are given in table 2. A typical value \( \tau_0 \approx 5 \times 10^{-14} \text{s} \) is observed, for the relaxation time, i.e. \( \tau_0^{-1} \) 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 \( T_{\text{max}} \), \( \Delta \varepsilon \) can be estimated from the area under the curve of tan δ versus \( T^{-1} \) [3]. From \( \Delta \varepsilon \), a value of \( \rho^2 N \) can be obtained, where
$p$ is an averaged dipole moment and $N$ is the concentration of dipoles. For instance, for sample 3, we find $p^2 N \sim 5 \times 10^{20}$ Debye$^2$ cm$^{-3}$ ($45 \times 10^4$ 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.

We thank Prof. Dr. J.M. Stevels for having stimulated this investigation.

References