X-ray photoelectron spectroscopy of alkali germanate glasses

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Several alkali germanate glasses of molar composition (100 − x)GeO2·xM2O (M = Na, with 0 ≤ x ≤ 35, or M = Cs, with 0 ≤ x ≤ 30) were prepared by melting, and their XPS spectra were recorded and analysed as a function of the alkali content. The simultaneous presence of bridging oxygen (BO) and non-bridging oxygen (NBO) atoms can be detected. In fact, XPS has proved to be a powerful technique for the quantification of BO and NBO atoms in glasses1 2 and has been employed successfully in the study of many oxide glasses.3 4

Alkali germanate glasses have been investigated by several authors in order to explain the so-called germanate anomaly. This anomaly manifests itself in the non-linear behaviour that some physical properties of germanate glasses show upon the addition of increasing alkali oxide contents: namely, the density and the refractive index of alkali germanate glasses exhibit maxima at ~15–20 mol. % M2O (M = Li, Na, K, Rb and Cs), with the actual compositions depending on the alkali species.5 Numerous structural studies have been carried out so far to elucidate the nature of this effect (see Ref. 6 and references therein) and two different structural models have been proposed.

Evstropiev and Ivanov7 suggested that this behaviour is a result of the conversion of Ge atoms from fourfold to sixfold coordination with increasing alkali oxide content and without the formation of NBO species up to the concentration region of maximum density and refractive index. Henderson and Fleet,8 who found no evidence of the occurrence of sixfold-coordinated Ge, proposed instead a ring model, in which three-membered rings with three distorted [GeO4] tetrahedra are formed, resulting in a more efficient packing of the inserted alkali ions. The debate on the correct structural model for alkali germanate glasses is still open and, in fact, some researchers have clearly identified the presence of NBO atoms at low alkali contents,9 10 even if sixfold-coordinated Ge atoms are present as well.

The present work is mainly focused on the characterization of sodium and caesium germanate glasses by XPS spectroscopy, and only one composition was investigated in the potassium and rubidium germanate glass systems. A large cation such as caesium and a small cation such as sodium were chosen in order to compare more easily the structural changes of GeO2 glass upon the insertion of different alkali ions. The XPS results for caesium germanate glasses are presented here for the first time, and a comparison with previous literature will be made in the case of the XPS results for sodium,9 11 potassium3 9 and rubidium3 10 germanate glasses. An estimate of the percentage of NBO species has been obtained through analysis of the XPS data, together with some indications concerning the role of the different alkali ions in the glass structure.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a technique mostly devoted to surface characterization but some conclusions can be extended further to the bulk structure, e.g. in the case of glasses where the presence of bridging oxygen (BO) and non-bridging oxygen (NBO) atoms can be detected. In fact, XPS has proved to be a powerful technique for the quantification of BO and NBO atoms in glasses1 2 and has been employed successfully in the study of many oxide glasses.3 4

EXPERIMENTAL

Sample preparation

Alkali germanate glasses were prepared with 0–30 mol. % Cs2O, 0–35 mol. % Na2O, 30 mol. % K2O and 30 mol. % Rb2O. Also, GeO2 plus Cs2CO3, Na2CO3, K2CO3 or Rb2CO3 compounds of reagent grade were mixed in powder form and melted in platinum crucibles in an electric
furnace at 1000–1400 °C, for 15–30 min. The melts were air quenched and the corresponding glasses were annealed at temperatures of ~50 °C below their glass transition temperature ($T_g$) for 30 min. Owing to some hygroscopicity, all the glasses were stored in a dessicator. Commercial GeO$_2$ powder (quartz crystalline form) was also used in order to compare with the data for pure GeO$_2$ glass.

**X-ray photoelectron spectroscopy**

The XPS measurements were carried out with a 310F Microlab instrument (VG Scientific) equipped with a concentric hemispherical analyser. Spectra were taken using non-monochromated Mg K$_\alpha$ radiation ($E = 1253.6$ eV) with 20 eV of pass energy, the energy resolution being ~1 eV. Some measurements of the as-prepared bulk glasses were carried out but mainly glass-powdered samples were analysed, with similar results. The glass samples were ground to a powder and placed on a gold foil with the use of silver glue. This allowed a constant check on the full width at half-maximum (FWHM) as a resolution reference and on the positions of the metallic Ag 3d$_{5/2}$ (368.27 ± 0.1 eV) and Au 4f$_{7/2}$ (84.0 ± 0.1 eV) lines. Because electrical equilibrium could not be achieved in the case of the present insulating samples, relative energies are the only reliable values. Nevertheless, a rough energy calibration of the XPS data was performed with reference to the C 1s line, present in all the XPS spectra, whose binding energy is 285 eV.

To assist in assigning complex profiles of the XPS spectra, deconvolution into components bands was performed using VG-specific software. The shape of the peaks was simulated using a mixed Gaussian–Lorentzian algorithm. No preconditioning was imposed on the FWHM, intensity and energy position of each peak, the only constraint being the relative position and separation of the peaks.

**RESULTS**

The glasses under investigation were preliminarily characterized by density, refractive index and DSC measurements, exhibiting the so-called ‘germanate anomaly’ in agreement with the existing literature. A vibrational characterization by infrared and Raman spectroscopies was also conducted. X-ray powder diffraction analysis indicated that the glasses prepared were completely amorphous.

The XPS wide-scan spectra for binding energies of 0–1200 eV and high-resolution spectra for the main peaks (O 1s, Ge 3d, C 1s, Au 4f and Ag 3d plus Na 1s, K 2p, Rb 3d or Cs 3d) were collected for all the samples. Silver, gold and carbon core-level peaks were recorded as a reference, whereas the oxygen and germanium core levels were analysed in detail. The XPS spectra of sodium germate glasses were similar to those in the literature. As a general observation, all O 1s peaks broadened with increasing alkali contents in the alkali germanate glasses, with the FWHM varying from a minimum of 1.8 eV to a maximum of ~2.8 eV. A series of oxygen peaks are superimposed in the literature for sodium, potassium and rubidium germanate glasses. Here, the Ge 3d peak was also found to broaden in sodium and caesium germanate glasses, with its FWHM varying from ~1.8 eV for pure GeO$_2$ glass to ~2.4 eV for the high-alkali glasses [see Fig. 1(b)].

It is well known that differences in the binding energy (BE) between BO and NBO atoms are lower in germanate glasses than in silicate glasses. The small energy difference between BO and NBO atoms, as well as the present energy resolution of ~1 eV, resulted in a very broad O 1s peak rather than two resolved peaks for the BO and NBO species. Only at 30 mol.% M$_2$O was some asymmetry evident in the O 1s peak, similar to other XPS data in the literature. However, other physical reasons also suggested the coexistence of two separate peaks below the O 1s curve, even when an asymmetry was not evident. In this regard, previous results of Raman spectroscopy on the same glasses showed evidence of significant concentrations of NBO species at ≥18 mol.% Na$_2$O and ≥15 mol.% Cs$_2$O besides, XPS peaks with FWHM values that were found to increase from ~1.8 eV up to ~2.8 eV are likely to involve more than a single transition. For this reason, a peak-fitting procedure was used, as explained in the experiment details. An example of these results is shown in Fig. 2. The percentage of the area below the lower BE component peak was taken as an estimate of the percentage of NBO atoms. All the results for BE values and the percentages of NBO atoms are listed for caesium and sodium germanate glasses in Tables 1 and 2.
2, respectively. The estimated error on the NBO percentage listed in Tables 1 and 2 was ~10%.

Some analysis was performed on the BE values. The differences in BE between O 1s (BO) and Ge 3d peaks were calculated and the values were constant for all glass compositions, within ±0.1 eV in most cases and ±0.4 eV at most (see Tables 1 and 2). The differences in BE of the alkali ion peaks and the O 1s or Ge 3d peaks were also calculated (see Tables 1 and 2). Data are somewhat spread for sodium germanate glasses, but some correlation is apparent in the caesium germanate glass data, where the BE differences appear to increase with increasing alkali contents.

In order to compare different alkali glasses with the same GeO2 content, the XPS spectra of 70GeO2:30M2O (M = Na, K, Rb and Cs) were collected and analysed. A general trend in the NBO concentrations was noticed: the O 1s peaks were again fitted with two contributing peaks, and percentages of NBO amounting to 24 ± 2%, 23 ± 2%, 26 ± 3% and 28 ± 3% were derived for the sodium, potassium, rubidium and caesium germanate glasses, respectively.

**DISCUSSION**

Some crystalline alkali germanates are known to contain both four- and sixfold-coordinated Ge atoms. One should

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**Table 1.** The XPS data for caesium germanate glasses, showing the results of XPS peak fitting for the O 1s peak

<table>
<thead>
<tr>
<th>x</th>
<th>BE (±0.2 eV)</th>
<th>FWHM (±0.2 eV)</th>
<th>%NBO</th>
<th>∆BE (O1s–Ge3d) (±0.2 eV)</th>
<th>∆BE (Cs3d–O1s) (±0.2 eV)</th>
<th>∆BE (Cs3d–Ge3d) (±0.2 eV)</th>
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</thead>
<tbody>
<tr>
<td>0(c-GeO2)</td>
<td>531.4</td>
<td>—</td>
<td>2.0</td>
<td>~0</td>
<td>498.9</td>
<td>—</td>
</tr>
<tr>
<td>0(v-GeO2)</td>
<td>532.2</td>
<td>—</td>
<td>1.8</td>
<td>~0</td>
<td>498.8</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>532.1</td>
<td>2.0</td>
<td>—</td>
<td>8 ± 1</td>
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<td>192.8</td>
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<td>531.7</td>
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<td>11 ± 1</td>
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<td>193.2</td>
</tr>
<tr>
<td>10</td>
<td>532.0</td>
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<td>2.0</td>
<td>8 ± 1</td>
<td>499.1</td>
<td>193.5</td>
</tr>
<tr>
<td>13</td>
<td>532.0</td>
<td>2.3</td>
<td>1.6</td>
<td>12 ± 1</td>
<td>498.9</td>
<td>193.5</td>
</tr>
<tr>
<td>15</td>
<td>532.0</td>
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<td>1.3</td>
<td>16 ± 2</td>
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<td>193.5</td>
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<td>18</td>
<td>531.3</td>
<td>2.2</td>
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<td>28 ± 3</td>
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<td>193.5</td>
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<td>1.7</td>
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<td>30</td>
<td>530.9</td>
<td>2.3</td>
<td>1.8</td>
<td>28 ± 3</td>
<td>498.9</td>
<td>193.6</td>
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Energy values in columns 1 and 2 are referenced to the C 1s peak (285 eV). Differences in XPS peak binding energies (∆BE) are also listed for all glass compositions.

**Table 2.** The XPS data for sodium germanate glasses, showing the results of XPS peak fitting for the O 1s peak

<table>
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<th>x</th>
<th>BE (±0.2 eV)</th>
<th>FWHM (±0.2 eV)</th>
<th>%NBO</th>
<th>∆BE (O1s–Ge3d) (±0.2 eV)</th>
<th>∆BE (Na1s–O1s) (±0.2 eV)</th>
<th>∆BE (Na1s–Ge3d) (±0.2 eV)</th>
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<tr>
<td>0 (c-GeO2)</td>
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<td>—</td>
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<td>498.9</td>
<td>—</td>
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<tr>
<td>0 (v-GeO2)</td>
<td>532.2</td>
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<td>1.8</td>
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<td>7 ± 1</td>
<td>498.9</td>
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<tr>
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<td>1.5</td>
<td>13 ± 1</td>
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<td>539.8</td>
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<tr>
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<td>15 ± 2</td>
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<tr>
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<td>2.0</td>
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<td>18 ± 2</td>
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<td>20 ± 2</td>
<td>499.1</td>
<td>539.8</td>
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<tr>
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<td>1.6</td>
<td>34 ± 3</td>
<td>499</td>
<td>540</td>
</tr>
<tr>
<td>35</td>
<td>530.9</td>
<td>1.8</td>
<td>1.6</td>
<td>34 ± 3</td>
<td>499</td>
<td>540</td>
</tr>
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Energy values in columns 1 and 2 are referenced to the C 1s peak (285 eV). Differences in XPS peak binding energies (∆BE) are also listed for all glass compositions.
also point out the occurrence of different polymorphs of crystalline GeO\(_2\) (c-GeO\(_2\)): quartz GeO\(_2\), with only fourfold-coordinated Ge atoms\(^1\), and rutile GeO\(_2\), with only sixfold-coordinated Ge atoms.\(^2\) The structure of the germania glass (v-GeO\(_2\)) has many similarities with the structure of silica glass (v-SiO\(_2\)), the v-GeO\(_2\) network being based on [GeO\(_4\)] tetrahedra.\(^3\) Nevertheless, the structures of silicate glasses exhibit a different behaviour upon the addition of alkali oxides in comparison with the corresponding germanate glasses. It is generally accepted that the addition of an \(M_2O\) molecular unit to the silica network creates two NBO atoms.\(^4\)

In alkali germanate glasses, on the other hand, two different mechanisms appear to compete upon addition of alkali oxide: the occurrence of higher coordinated Ge atoms and the formation of NBO species. Based on XPS data, Smets and Lommen\(^5\) have estimated 37 ± 3\% and 38 ± 3\% NBO atoms in silicate glasses with 30 mol.\% \(K_2O\) and 30 mol.\% \(Na_2O\), respectively, and 29 ± 3\% and 28 ± 3\% NBO atoms in germanate glasses with 30 mol.\% \(K_2O\) and 30 mol.\% \(Na_2O\), respectively. Also, a value of 25 ± 2\% NBO was given by Gee et al.\(^6\) for germanate glasses with 30 mol.\% \(Na_2O\), whereas a substantially lower value of only ~15\% NBO was evaluated by Lu et al.\(^7\) for germanate glasses with 24.7 mol.\% \(K_2O\). Our present results for germanate glasses containing 30 mol.\% \(M_2O\) are thus in agreement, within the error bars, with most of the literature and suggest that up to 30 mol.\% \(M_2O\), the germanate and silicate glass systems are still not isostructural. We also noted a slight increase in the NBO concentration of the alkali germanate glasses in the order Na \(\rightarrow\) K \(\rightarrow\) Rb \(\rightarrow\) Cs-germanate, which is in agreement with an increase in the modifying character of the alkali ions with their ionic radii.

Concerning the observed differences in BE values (Tables 1 and 2), it appears that Cs\(^+\) cations are distributed in the germanate network in a more homogeneous fashion compared with Na\(^+\) cations, because the values of caesium germanate glasses appear to follow a trend whereas the data of sodium germanate glasses were considerably spread.

Regarding the Ge 3d data, the steady increase in the FWHM might indicate the progressive simultaneous occurrence of multiple coordination sites for Ge. However, the absence of a maximum FWHM at ~15–20 mol.\% \(M_2O\) did not support the occurrence of a maximum concentration of higher coordinated Ge atoms in that composition range.

Our results indicating the appearance of NBO atoms for both sodium and caesium germanate glasses at low alkali concentrations are in apparent disagreement with the previous literature for sodium germanate glasses. In fact, Smets and Lommen,\(^3\) following the model of Verweij and Buster,\(^8\) supported the existence of NBO species only for glasses containing >18 mol.\% \(M_2O\) and they reported just 4 ± 3\% NBO atoms for 20 mol.\% \(K_2O\), whereas Gee et al.\(^6\) found no NBO atoms for 18 mol.\% \(Na_2O\). This is in contrast both with our XPS data and with the Raman spectroscopy results, which yielded significant concentrations of NBO species at 18 mol.\% \(Na_2O\).\(^9\) Concerning the present new results on caesium germanate glasses, they appear to be in agreement with the existing literature on rubidium germanate glasses\(^10\) and are again supported by our previous Raman data.\(^11\) Thus, we suggest that higher coordinated Ge atoms are indeed present in the low-alkali germanate glasses, and we would also like to stress that such glasses (below ~18 mol.\% \(M_2O\)) also contain significant concentrations of NBO atoms.

CONCLUSIONS

The occurrence of significant concentrations of NBO atoms at <18 mol.\% \(M_2O\) is suggested for sodium and caesium germanate glasses; the percentages of NBO species are, in any case, lower than those in the corresponding silicate glasses and the occurrence of Ge atom coordinations higher than four in alkali germanate glasses is likely. In addition, a different behaviour of the Na\(^+\) and Cs\(^+\) ions has been evidenced, indicating a stronger network-modifying character of Cs\(^+\) compared with Na\(^+\). A tendency was noticed for the formation of larger concentrations of NBO atoms in Cs-germanate glasses compared with their Rb-, K- and Na-germanate counterparts.

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