The transport of potassium and rubidium ions through glasses containing the respective alkali ion as mobile species has been investigated by means of bombardment induced ion transport (BIIT) and impedance spectroscopy (IS). The conductivities as well as the activation energies derived from the two approaches are in agreement lending further support to the recently developed BIIT approach.

**Ion conductivity; electrodiffusion**

I. **INTRODUCTION**

Recently, we have developed a new technique, which allows to induce and to measure ion transport through a wide range of materials under conditions of a single sample/electrode contact. The technique was termed bombardment induced ion transport (BIIT) since the ion transport of interest was induced by shining a continuous ion beam at a sample surface [1]. Attachment of the ions to the surface causes a surface potential and a surface charge density. A grounded metal electrode connected to the backside of the sample ultimately defines a potential gradient across the sample, which is inherently also accompanied by a concentration gradient. These gradients induce ion transport through the sample which is detected as a current at the backside electrode. So far we have demonstrated the viability of the BIIT approach for ion conducting glasses [2] as well as polymer films [3]. If the focus of interest is on the macroscopic conductivity of an ion conducting glass, the choice is to employ the same alkali ion for bombardment which is the carrier of charge transport in the glass. This intuitive condition is meaningless when investigating alkali ion transport through a polymer film, which does not contain the alkali ion in the beginning. In that case the BIIT experiment (when operated for a sufficiently long time) will lead to the formation of an electrodiffusion profile [4]. Such a diffusion profile does not evolve if e.g. a potassium ion conducting glass is bombardment with a potassium ion beam. However, if we bombard a sodium ion conducting glass with a potassium ion beam, an electrodiffusion profile evolves for the sodium which is replaced by the potassium ions [5]. Since under such conditions potassium ions and sodium ions coexist over a spatial zone spanning on the order of 100 nm, one hopes that such experiments may contribute to the understanding of the mixed alkali effect [6-8].

Ultimately one would aim at experiments on a type of glass for which two variants can be prepared, one conducting alkali ion A1 and one conducting alkali ion A2. Consequently one can think of two different BIIT experiments, i. one where the ion conducting glass is bombarded with the same alkali ion, which would yield the conductivities, and ii. the cross-wise bombardment with the respectively other alkali ions which would yield the diffusion profiles. It is the aim of the current contribution to set the stage for the first part of the challenge, part i.

In order to reach the goal stated above, we need to identify a glass system, which first of all is chemically and mechanically stable and secondly ensure that the relevant conductivities are within the accessible detection range. As such a glass system we have identified the calcium-phosphate glasses, which have attracted interest because of the potential for medical application [9]. These glasses can be prepared with alkali ions of our choice, which will ultimately be the mobile species in that glass.

II. **EXPERIMENTAL APPROACH**

The BIIT experiments have been performed under high vacuum conditions at a working pressure of less than $2 \times 10^{-6}$ mbar. The setup consists of a thermionic ion emitter (1), a system of electrostatic lenses (L1-L6) used for guiding the ions and the sample holder (3) including the sample (2). A sketch of the setup is given in Fig. 1.

As thermionic emitter a synthetic leucite (KAlSi2O6) or Rb-leucite (RbAlSi2O6) pellet is used that is heated to about 850 °C. The leucite has been mixed with molybdenum in a ratio of 1:4 to improve the emission properties of the emitter. In front of the emitter, a strong electric field of -2 kV/cm abstracts the ions and leads to a continuous ion beam such that ion currents up to 2 µA can be reached.

![Figure 1. Scheme of the experimental setup.](image-url)
The kinetic energy of the ions is determined by setting appropriate voltages to the repeller lens L0. The subsequent lens system focuses and guides the ions toward the glass sample position where the ions impinge on the glass surface. By slowly increasing the repeller voltage, direct implantation of the ions is avoided. The ions are softly attached to the front side of the glass sample and give rise to a concentration and a potential gradient across the glass [1,2]. The ion current flowing through the glass is detected at the backside of the glass via a glued metal electrode, subsequently A/D converted and processed in a computer. After some seconds a quasi stationary situation establishes where the ion current detected at the backside electrode becomes time independent. Under these conditions, the same amount of carriers is attached to the glass surface as is neutralized at the backside electrode and the potential at the glass surface is determined by the kinetic ion energy. The ion currents discussed in this manuscript are recorded in this limit. The specific conductivity can finally be determined by recording the current at the detection electrode as a function of the kinetic ion energy. At low kinetic ion energies a linear increase of the ion current as a function of the kinetic ion energy is observed with a slope that is given by the resistance of the glass. Eventually, the specific conductivity is calculated by taking into account the glass thickness and the bombarded area of the sample.

The AC impedance spectroscopy (IS) measurements have been performed in a temperature range between 30 °C to 240 °C controlled by a Novocontrol Quadro Cryosystem. Additionally, a Novocontrol Alpha-AK impedance analyzer has been used to control the applied voltage and the ac frequency. The voltage applied has been 0.5 V (rms) while the AC frequency has been set to values between 0.01 Hz and 1 MHz. Ultimately, the DC plateau is analyzed for deriving the AC frequency. The thermo analysis of the glass samples has been carried out using a differential scanning calorimeter (Mettler-Toledo, DSC 1 – Sensor: HSS7). To this end, some milligrams of the sample material have been mortared in an agate mortar and were subsequently pressed into an aluminum crucible. As reference an identical aluminum crucible has been used. Both crucibles have been heated twice between 100 °C and 500 °C at a rate of 10 K/min and were subsequently cooled. The experiments have been carried out under a nitrogen atmosphere.

The density of the glasses was obtained by applying the Archimedean principle. In order to determine the mass of the sample a high precision balance (Mettler-Toledo, XS105DualRange) has been used. The accuracy of the balance is ±0.02 mg. The glass density has eventually been determined using a pycnometer (Brand) with an accuracy of ±0.001 mg/cm³. Every glass density has been determined three times. The standard deviation of these measurements has been ±0.06 mg/cm³.

### III. RESULTS AND DISCUSSION

In order to characterize the investigated glasses, the glass transition temperature and the mass density ρ of each glass has been measured. The results are given in table 1 where also the calculated alkali ion density ρ(M) is given. For completeness, the thickness d of the glass sample that is used in the BIIT experiment is given.

One obtains that the glass transition temperature increases with increasing CaO-content. This observation is reasonable as the CaO acts as a network modifier oxide and links the phosphate chains. The larger the amount of CaO, the more cross links are present between the phosphate chains [11]. The cross links stabilize the glass and lead to a higher viscosity and eventually to a higher glass transition temperature. The mass density of the glasses can be motivated by comparing the densities of the educts [12,13]. For the potassium glasses, the K₂O has a lower mass density (2.35 g/cm³) than the CaO (3.34 g/cm³). In the case of the rubidium glasses the situation is converse. Here, the Rb₂O has the higher mass density (4.00 g/cm³). As a consequence, it is expected that the mass density of the potassium glasses should increase with increasing CaO content while the mass density of the rubidium glasses is decreasing with increasing CaO content. As table 1 shows the measured glass densities follow the expected trend. From the mass density and the stoichiometry of the glass it is possible to calculate the mobile ion density of the glasses, e.g. the density of the alkali ion.

<table>
<thead>
<tr>
<th>Glass</th>
<th>d (µm)</th>
<th>Tg (°C)</th>
<th>ρ (g/cm³)</th>
<th>ρ(M) (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca20K</td>
<td>799</td>
<td>338</td>
<td>2.498±0.01</td>
<td>9.75E+021</td>
</tr>
<tr>
<td>Ca30K</td>
<td>535</td>
<td>401</td>
<td>2.56±0.01</td>
<td>7.35E+021</td>
</tr>
<tr>
<td>Ca20Rb</td>
<td>955</td>
<td>318</td>
<td>3.07±0.06</td>
<td>9.22E+021</td>
</tr>
<tr>
<td>Ca30Rb</td>
<td>571</td>
<td>418</td>
<td>2.914±0.004</td>
<td>6.89E+021</td>
</tr>
</tbody>
</table>
It is found that the ion density in the rubidium glasses is about 5 percent lower than the mobile ion density in the potassium glasses. Hence, we can conclude that the rubidium widens the glass structure compared to the potassium glasses most probably due to its larger ion radius.

One of the most important quantities that characterize the ion transport through a glass is the specific conductivity. Generally, all mobile charge carriers of the glass contribute the specific conductivity. For the current glass system the ionic conductivity is known to be much larger than the electronic conductivity in the investigated temperature regime. Additionally, from Time-of-Flight Secondary Ion Mass-Spectrometry investigations on bombarded calcium phosphate glasses, it is known that the calcium ions are basically immobile \[5\]. As a consequence, the alkali ion is the only charge carrier that significantly contributes to the conductivity. Often, the specific conductivity of a glass obeys an Arrhenius law

\[
\sigma_{\text{spec}} = \sigma_0 \exp \left( - \frac{E_{\text{act}}}{k_B T} \right), \quad (1)
\]

where \( E_{\text{act}} \) is the activation energy and \( k_B T \) is the Boltzmann’s constant times the temperature. The constant \( \sigma_0 \) contains the mobility of the ions and the mobile ion density. In order to connect the structure information to the ion transport properties of the glasses, we detect the specific conductivity of the glasses as a function of the sample temperature using two independent techniques, the BIIT and the IS.

In the framework of the BIIT technique, we bombard the glass with the alkali ion species that is native to the glass, i.e. a CaXK glass is bombarded with K\(^+\) ions and a CaXRb glass is bombarded with Rb\(^+\) ions. The temperatures applied during the BIIT experiments were between 35 °C and 125 °C. The repeller voltage was varied between 15 V and 100 V. The ion current that reached the glass surface was about one order of magnitude higher than the maximally detected backside current, which guaranteed that the bombarded glass surface was homogeneously charged \[1,2\]. The sample thicknesses are listed in table 1.

Figure 2 shows the specific conductivity of the two potassium glasses in an Arrhenius plot. The specific conductivities measured via BIIT (filled symbols) are compared to respective data from IS (open symbols). Very good agreement between the two methods is observed both in terms of absolute conductivity as well as in term of the activation energy, which is derived from the slope of the curves. For the Ca20K, we find \( E_{\text{act}}(\text{BIIT}) = 0.84 \text{ eV} \pm 0.02 \text{ eV} \) and \( E_{\text{act}}(\text{IS}) = 0.91 \text{ eV} \pm 0.02 \text{ eV} \). For the Ca30K glass, we find \( E_{\text{act}}(\text{BIIT}) = 0.96 \text{ eV} \pm 0.02 \text{ eV} \) and \( E_{\text{act}}(\text{IS}) = 1.04 \text{ eV} \pm 0.02 \text{ eV} \). The fact that the IS value for \( E_{\text{act}} \) is larger than the BIIT values is connected to the temperature range extending to significantly higher values for the IS setup. In all measurements we observe a slight increase of the activation energy with increasing temperature. Although an interesting detail, this is not at the heart of the current investigation.

At 100 °C, the conductivity of the Ca20K is about two orders of magnitude larger than the conductivity of Ca30K (compare table 2). This difference is partially due to the larger density of alkali ions in the Ca20K (compare table 1). On the other hand, the potassium ion density in the Ca30K is only about 25 percent lower than that in the Ca20K glass. Hence, the different ion density can explain only a small fraction of the conductivity difference. Most of the difference originates from the different diffusion coefficients in the two glasses. The Ca30K glass has the higher CaO content and thus exhibits more cross links. These cross links lead to a less flexible glass structure such that structure is hardly modified if an ion jumps from side to side. In contrast the Ca20K structure may respond more flexible to jumps of the ions such that the activation energy for the ion transport is lower in this case. Additionally, as the Ca20K shows less cross links there may be more paths for the ion movement available. Both effects lead to a larger diffusion coefficient in the case of Ca20K. Here, the diffusion coefficients can be calculated from the specific conductivities using the Einstein relation

\[
D = \frac{k_B T}{q \rho (M)} \sigma_{\text{spec}}, \quad (2)
\]

where \( q \) is the ion charge. The values derived for the diffusion coefficient are given in table 2.

In a second step, specific conductivities have also been measured for the corresponding rubidium glasses. The results are shown in Fig. 3, again in the form of an Arrhenius plot, where the data detected via BIIT are shown as filled red symbols while the open black symbols represent the IS data.

Figure 2. Arrhenius plot for the CaXK glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>( \sigma_{\text{spec}} ) (Scm(^{-1}))</th>
<th>( D ) (cm(^{2})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca20K</td>
<td>1.19E-10</td>
<td>2.44E-15</td>
</tr>
<tr>
<td>Ca30K</td>
<td>1.70E-12</td>
<td>4.65E-17</td>
</tr>
<tr>
<td>Ca20Rb</td>
<td>1.75E-10</td>
<td>3.80E-15</td>
</tr>
<tr>
<td>Ca30Rb</td>
<td>3.92E-13</td>
<td>1.14E-17</td>
</tr>
</tbody>
</table>

TABLE II. SPECIFIC CONDUCTIVITY AND DIFFUSION COEFFICIENT OF THE CaXK AND THE CaXRb-SERIES, ALL DATA AT 100 °C.
The conductivity of Ca20Rb is shown as triangles while the Ca30Rb data are presented at squares. We observe again very good agreement between the IS and the BIIT measurements. For Ca20Rb, we find an activation energy of $E_{\text{act}}(\text{BIIT}) = 0.80 \pm 0.02 \text{ eV}$ and $E_{\text{act}}(\text{IS}) = 0.84 \pm 0.02 \text{ eV}$. For the Ca30Rb glass, we find $E_{\text{act}}(\text{BIIT}) = 1.05 \pm 0.04 \text{ eV}$ and $E_{\text{act}}(\text{IS}) = 1.04 \pm 0.02 \text{ eV}$. Similar to the potassium glass the increase of the CaO concentration leads to higher activation energies. However, for the rubidium glasses this effect is even stronger than for the potassium glasses. The reason might be that rubidium ions have a larger ion radius and a more rigid glass structure may inhibit the ion transport of the larger ions more effectively. This interpretation is supported by the diffusion coefficient of Rb\(^+\) in the Ca30Rb which is about 4 times smaller than that of K\(^+\) in Ca30K (compare table 2). In the less cross linked Ca20M glasses an opposite effect is observed. Here, the rubidium glass shows a larger diffusion coefficient. One could speculate that in the case of a weakly cross linked glass the larger rubidium ion radius leads to an effective widening of the glass structure such that the ion transport is supported. The lower activation energy is also fostering this interpretation.

IV. SUMMARY

We have investigated the transport of potassium ions and rubidium ions through calcium-phosphate glasses containing varying amounts of the respective alkali ions as mobile species. Conductivities as well as activation energies have been determined by means of BIIT and IS. Results from the two techniques are in good agreement. Additionally, the mobile ion densities in the glasses have been calculated via the mass density and the stoichiometry of the glasses.

Investigating the temperature dependent specific conductivities, we were able to determine the activation energy for the DC transport of the ions. In both series of alkali conducting glasses an increasing amount of CaO leads to larger activation energies. With decreasing density of the mobile ions the average separation of these cations increases, which leads to a less strong overlap of the coulomb potential [14]. In this case the cations have to overcome a higher energy barrier to jump to the next cation site.

From the ion density and the specific conductivity the diffusion coefficient in each glass could be determined. The diffusion coefficients are smaller for larger CaO content which may be explained by the higher degree of cross linking of the phosphate network. This effect is obviously stronger in the rubidium glasses most likely due to the larger ion radius of rubidium compared to potassium.

For the future we plan to complement the investigation presented here with a cross-wise BIIT experiment where the rubidium conducting glasses are bombarded with potassium ions and vice versa. This is the subject of ongoing work.

V. ACKNOWLEDGMENT

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VI. REFERENCES