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Transport properties of the sodium-yttrium-silicate glasses

G.V. Nechaev [a], S.G. Vlasova [b], I.S. Kovyazina [b,*], O.G. Reznitskich [a]

[a] Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia
[b] Ural Federal University named after the first President of Russia B.N. Yeltsin, Ekaterinburg, Russia

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ABSTRACT

The influence of yttrium oxide on the transport properties and chemical stability of sodium silicate glasses is investigated. The seven sodium-yttrium silicate glass compositions were synthesised. There are three composition with $Na_2O/Y_2O_3 = 6.5$ and four with permanent Na_2O content with 5 to 8 mol% of Y_2O_3. The thermal behaviour of the glasses was studied with dilatometric and DSC methods. The research into the electrical characteristics of the glass has shown that their electrical conductivity is in the range of 5×10^{-8}–10^{-6} S/cm at 25 °C and 10^{-3} S/cm at 300 °C. It is shown that the hydrolytic resistance increases when growing the Y_2O_3 concentration in the glass composition at constant Na_2O content.

1. Introduction

Lithium and lithium-ion battery technology, widely used in portable electronic devices, has significantly improved over the last 20 years. Nevertheless, recently there has been an increase in attention for novel types of sodium batteries. The substitution of sodium for lithium has the following advantages. Firstly, sodium is the one of the most abundant elements on the earth, which is beneficial in terms of availability and cost reduction of high capacity batteries. Secondly, cheaper materials for current collectors and liquid organic electrolytes can be made available for sodium and sodium-ion batteries [1]. The advantages of sodium batteries are most obvious when in practical use within high-power devices such as electrochemical storage devices for load balancing in power transmission applications and high-power batteries for electric vehicles. A key issue in the further improvement of the sodium batteries, both high- and low-temperature, is the creation of a new solid electrolyte separator [1,2], since the currently used β-alumina membrane has a number of disadvantages, including the complexity of the synthesis and scarcity of the raw materials. As a result, sodium-conducting solid electrolytes are currently the subject of intensive studies as a means of creating an alternative to β-alumina in sodium current sources [1–2]. Potential alternatives under consideration include amorphous solid electrolytes of both glassy and glass-ceramic types.

The glassy solid electrolyte structure successfully combines high disordering of the mobile alkali metal ion sublattice and a high concentration of mobile ions that are weakly bound to the anionic framework, i.e. it fully meets the requirements for high electrical conductivity in solids. The technological advantages of glassy electrolytes can be listed in terms of their nonporous nature, greater strength and simplicity of processing, giving them the possibility of being miniaturised and fabricated into thin films. Previously, a number of authors [3–5] considered sodium borosilicate glass as the most suitable substance for use in solid electrolyte sodium-sulphur cells. Currently, glass and glass-ceramic-based Na_2S–P_2S_5 systems provide superior transport properties for amorphous sodium between conductors (10^{-5} S/cm at 25 °C, 8×10^{-2} S/cm at 300 °C [6]), which allows it to be used as a solid electrolyte in low temperature sodium batteries. As a result of a series of studies on glass-ceramic electrolytes in the Na_2O–Y_2O_3–SiO_2–P_2O_5 system carried out by the Yamashita Group at the University of Tokyo, electrolytes were obtained with a conductivity of ~10^{-1} S/cm at 300 °C [7–9]. However, a significant disadvantage of thiophosphate glasses is their extreme sensitivity to oxygen and moisture, reducing their applicability in sodium-air batteries despite the development of the latter having recently received much attention [1, 10–11].

Among the sodium glasses described in the literature it is possible to identify a number of compositions having sufficiently high transport properties [3]. In particular, these include Na_2O–SiO_2 and Na_2O–SiO_2–B_2O_3 systems having a high Na_2O content (up to 50 mol%) and containing a modifier such as sodium halide. However, all these glasses have a notably low chemical resistance, which limits their practical use. One means of improving the stability of sodium silicate glasses is the introduction of a stabiliser, namely rare earth or transition metal oxides. In

* Corresponding author at: Ural Federal University, 28, Mira Str., Ekaterinburg, Russia.
E-mail address: Inna12.03@yandex.ru (I.S. Kovyazina).

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particular, to improve chemical resistance and reduce the propensity for the crystallisation of phosphate glasses, alumina has successfully been used [12,13], the use of which has improved the hydrolytic stability and electrical conductivity of glass.

According to some authors [3,14], the basicity of input stabiliser oxide has a significant influence on their conductivity. Yttrium oxide has the highest basicity value in comparison with Al_2O_3 [14];this gives a reason to expect an improvement not only in chemical resistance, but also in the transport properties of the glasses in the Na_2–Y_2O_3–SiO_2 system as compared with the sodium silicate system.

Data on the properties of sodium-yttrium-silicate glasses in the literature is scarce [15–17]. On the basis of glass studies with different content of Li_2O, Na_2O, Y_2O_3 and SiO_2, Alexander and Riley [15] assumed that the most optimal ratio in terms of glass conductivity is $Na_2O/Y_2O_3 = 6.5$. However, we were not able to find further experimental confirmation of this in the literature. At the same time, glasses of the Na_2O–Y_2O_3–SiO_2 system have significant interest for practical use due to their high chemical stability and electrical conductivity. Thin glass films fabricated from conducting sodium glasses may be applied as membranes for the division of cathode and anode parts of sodium-air batteries. Moreover, glassy ion-exchange membranes are used in analytical and biochemical research of ion-selective electrodes. However, further research of the sodium-yttrium-silicate glasses is necessary in order to identify glass compositions having optimal conductivity and chemical stability properties.

The aim of the present research is to study the properties of the four glass compositions having different sodium oxide and yttrium content at a ratio constantly equal to 6.5. This ratio was selected on the basis of the assumption of the authors [15] that this molar ratio is optimal for electrical conductivity. Furthermore, in order to clarify the influence of yttrium oxide on the properties of glasses, four glass compositions with constant Na_2O and variable Y_2O_3 contents were investigated. The compositions of the glasses studied in our work are shown in Table 1.

2. Materials and experimental methods

2.1. Synthesis of sodium-yttrium-silicate glasses

Starting reagents for the glass synthesis were Na_2CO_3 (99.9%), Y_2O_3 (99.9%) and SiO_2 (98%). All reagents were pre-dried to a constant weight and then mixed in stoichiometric amounts. The batches were calcined at 900 °C in an electric furnace and then melted in a platinum crucible at the temperature range of 1400–1500 °C. The resulting melt was poured into a graphite mould, making rods (size $50 \times 10 \times 10$ mm). The rods were then annealed at the appropriate temperature, determined by differential thermal analysis (DTA).For further characterisation and analysis, glass bars (~40 mm length) or glass plates of 1–2 mm thickness were cut and polished.

Table 1
Chemical compositions, basicity (Λ) and characteristic temperatures of the investigated glasses (°C): glass transition temperature (T_g), softening point (T_w) of glass, crystalline phase formation temperature (T_c) and coefficients of thermal expansion (α). T_g,T_w, T_c and α values are obtained from experimental measurements.

No	Composition, mol%	Λ	T_g	T_w	T_c	$\alpha_{573-673\ K}$ ($*10^{-6}\ K^{-1}$)
1	$35Na_2O$–$5.3Y_2O_3$–$59.7SiO_2$	0.646	572	602	876	15.3
2	$40Na_2O$–$6.1Y_2O_3$–$53.9SiO_2$	0.674	568	575	865	16.8
3	$45Na_2O$–$6.8Y_2O_3$–$48.2SiO_2$	0.704	562	591	768	18.1
5	$37.9Na_2O$–$5Y_2O_3$–$57.1SiO_2$	0.659	549	600	862	14.8
6	$37.9Na_2O$–$6Y_2O_3$–$56.1SiO_2$	0.663	569	601	833	15.1
7	$37.9Na_2O$–$7Y_2O_3$–$55.1SiO_2$	0.667	593	641	779	15.7
8	$37.9Na_2O$–$8Y_2O_3$–$54.1SiO_2$	0.671	626	679	775	14.9

2.2. Chemical and structural characterisation

The chemical composition of the synthesised samples was confirmed by atomic absorption spectroscopy (ICAP 6300 spectrometer with an accuracy of 0.5–0.7 wt.%). X-ray diffraction analysis was performed using a Rigaku D/Max 2200 Powder X-ray Diffractometer with a Cu $_{K\alpha}$-radiation device (1.5418 Å) having scanning angle intervals between 10° and 80°.

2.3. Physical properties

The glass transition temperatures (T_g), softening point (T_w) of glasses and crystalline phase formation temperatures (T_c) and the coefficients of their thermal expansion were determined using dilatometric and differential scanning calorimetry (DSC) methods. Dilatometric measurements were performed using a NETZSCH DIL 402 C dilatometer, with samples in the form of bars of 40 mm length. Thermal analysis (DSC) was carried out with the NETZSCH STA 449 *F*1 instrument in the temperature range of 35–1000 °C with the heating rate of 10 °C/min. The electrical conductivity of the glasses was determined by the electrochemical impedance method using the AUTOLAB PGSTAT 302N instrument. Glass plates of ~1 cm^2 with a thickness of 1.5 mm were used. The plates were coated with platinum electrodes by vacuum deposition. Conductivity for each sample was calculated from the resistance values (R), obtained from the intersection points of the low frequency portion with the axis of the real resistance and the geometrical dimensions of the sample according to the formula: $\sigma = d/(R \times S)$, where S = area of the electrode, d = thickness of the sample and R = the resistance. The conductivity measurement error did not exceed 10%. Conductivity measurements were performed in the temperature range of 25–300 °C.

2.4. Hydrolytic resistance characterisation

The hydrolytic resistance of glasses was determined by exposing the glass to 100 ml of distilled water for 1 h at 95 °C. Prismatic samples ($5 \times 8 \times 3$ mm) were cut from the annealed glass rods. After cleaning in ethanol, the samples were dried at 70 °C until they reached a constant weight (10^{-4} g weighing precision). The dissolution rate (D_r) was determined by the weight loss (Δm) of the sample with reference to the surface area (S) and the water exposure time (t, 60 min): $D_r = \Delta m/(S \times t)$.

3. Results and discussion

3.1. Chemical and structural characterisation

The chemical analysis of the synthesised glasses has confirmed the compliance of the calculated and derived compositions. Excepting the composition No 4 [$50Na_2O$–$7.6Y_2O_3$–$42.4SiO_2$], the X-ray patterns presented only a halo with no lines of any crystalline phase detected. This fact indicates that glass compositions No 1–3 and 5–8 had amorphous structure. Composition No 4 samples had become opaque on cooling. This indicates a crystallisation process in this glass composition. X-ray analysis has shown the presence of crystalline phases in these composition samples. These phases were identified as sodium-yttrium silicates $Na_3YSi_2O_7$ and $NaY_9Si_6O_{26}$.

3.2. Physical properties

The dilatometric curve and DSC curve of glass composition No 1 [$35Na_2O$–$5.3Y_2O_3$–$59.7SiO_2$] are depicted in Figs 1 and Fig. 2 respectively. The DSC curves and dilatometry of the other studied glasses have a similar appearance. Characteristic temperatures of the investigated glass compositions, such as the glass transition temperature (T_g), the softening point of the glass (T_w), the crystalline phase formation