

Density, Viscosity and Electrical Conductivity of the Molten Cryolite Electrolytes ($\text{Na}_3\text{AlF}_6\text{-SiO}_2$) for Solar Grade Silicon (Si–SoG) Electrowinning

Michal Korenko · Zuzana Vasková · Jozef Priščák · František Šimko · Marta Ambrová · Zhongning Shi

Received: 23 January 2014 / Accepted: 17 June 2014 / Published online: 2 July 2014
© Springer Science+Business Media Dordrecht 2014

Abstract Density, viscosity and electrical conductivity of the molten system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ have been investigated in the concentration range up to 50 mole % of SiO_2 . Density was measured by means of a computerized Archimedean method, viscosity of the melt by computerized torsion pendulum method and the electrical conductivity by means of the tube–cell (pyrolytic boron nitride) with stationary electrodes. It was found that the density, viscosity and conductivity vary linearly with the temperature in all investigated mixtures. On the basis of the density data, the molar volume of the melts and the partial molar volume have been calculated.

Keywords Solar grade silicon (Si–SoG) · Silicon electrolysis · Molten salts · Density · Viscosity · Electrical conductivity

1 Introduction

In a few weeks in 1905, while working in a Swiss patent office, Albert Einstein wrote five papers that completely changed the world. One of the papers unlocked a potential

of nuclear energy (mass–energy equivalence), another one laid a basis for the photovoltaics (photoelectric effect).

Solar power energy is the most prevalent form of a renewable energy. It is not yet apparent what portion of our energy needs will be ultimately based on the sunshine, although it has a potential to definitely far transcend the total energy demand of the humankind on the globe. One of the recent obstacles against solar power energy becoming a greater contributor to the energy basket is its high price. Silicon, remaining the major photovoltaic stuff, accounts for 25–50 % of the cost of solar modules [1] hence a strong regard has been paid to the manufacture of a so-called solar grade silicon (Si–SoG) at lower cost. Although cost of the solar-cells is continuously decreasing, it is not always cheaper in relation to the usual ways of the electricity generation, e.g. fossil fuel or nuclear power.

The rather high price of solar grade silicon (Si–SoG) caused by a limited supply, has thus met the high setback of the photovoltaic industry instead of its much anticipated growth. Therefore it is crucial to elaborate a method for the synthesis of Si–SoG that is energy efficient and will deliver a competitive feedstock material. As a hopeful concept, the electrodeposition of silicon from molten fluorides–based electrolytes at relatively low temperatures (around 1000 °C), alike to the Hall–Héroult process for industrial aluminium production, has been investigated by various researchers [2, 13].

Former research between several molten salt electrolytes has revealed that the cryolite–based systems might be satisfactory for the electrowinning of silicon with respect to the deposited material purity and process current efficiency [8, 9]. But the process has not been commercialized successfully up-to-date due to the rather high melting point of silicon (1414 °C) that avoids the formation of liquid silicon at the electrolysis temperature of 1000 °C. In addition, a

M. Korenko · Z. Vasková (✉) · J. Priščák · F. Šimko
Institute of Inorganic Chemistry, Slovak Academy of Sciences,
Dúbravská cesta 9, 845 36 Bratislava, Slovakia
e-mail: zuzana.vaskova@savba.sk

M. Ambrová
Institute of Inorganic Chemistry, Technology and Materials,
Slovak University of Technology, Radlinského 9,
812 37, Bratislava, Slovakia

Z. Shi
Materials and Metallurgy School, Northeastern University (NEU),
Wenhua Road 3-11, 110819, Shenyang, China

precise understanding of the physico–chemical behavior of different cryolite–based electrolytes, which is primary for industrial application, is also very limited [6, 7, 14, 16].

The present paper is a part of the larger project undertaken to obtain the primary physico–chemical properties like density, viscosity, electrical conductivity, vapor pressure and surface properties of different fluoride melts (containing silicon species), mainly based on the systems cryolite (Na_3AlF_6) – silica (SiO_2). The final object is thus to obtain a base for the physico–chemical description of the molten electrolytes needed for a future electro-winning of Si–SoG.

Although physico–chemical behavior of the various molten cryolite systems is the subject of a longtime inquiry due to the Hall–Héroult technology, data regarding the physico–chemical properties of the particular system Na_3AlF_6 – SiO_2 are not only rather limited, but also available only for a small concentration range of silica. There are just a few data concerning the density [6] and electrical conductivity [7, 14, 15], and no data of viscosity. Moreover, the authors in work [6] reported just the data of the industrial cryolite electrolytes for the Hall–Héroult electrolysis process (cryolite with alumina and other additives). In this paper, the experimental data of a density, viscosity and electrical conductivity of molten Na_3AlF_6 – SiO_2 mixtures are presented.

2 Experimental

2.1 Chemicals

Synthetic cryolite (NaF – AlF_3 eutectic) was taken for preparing the experiments (AlF_3 sublimated under low pressure (ca 100 Pa at 1100 °C). Compounds of analytical grade NaF (Fluka™) and SiO_2 (Johnson Matthey Chemicals™, U.K.) were used. For determination of the cell constant, a “specpure” NaCl and KCl (Johnson Matthey Chemicals™, U.K.) were used. All chemicals (except a sublimated AlF_3) were dried in a vacuum oven at 400 °C for several hours before the melting.

2.2 Density

The density of the investigated systems has been measured using a computerized Archimedean method under the dried nitrogen atmosphere. A platinum sinker, suspended in a platinum wire connected below an electronic balance, has been used as the measuring corpus. Temperature dependency of the sinker’s dilatation has been identified by a calibration using molten NaCl and KF (analytical purity). Temperature has been monitored by a Pt–Pt10Rh thermocouple. A particular amount of the investigated mixture

was placed into a platinum crucible and introduced into a resistance furnace. Deepness of the immersion was directed using a platinum electrical contact. Experiments were performed in a temperature range according to the temperature of primary crystallization of each measured mixture. Measured samples were heated to the upper temperature then the chilling was performed down to the lowest temperature. Results of the density were automatically recorded every 3 s for each system. A detailed description of the apparatus can be found elsewhere [17].

2.3 Viscosity

The computerized torsion pendulum method based on the measurement of a logarithmic decrement of attenuation, due to the friction in the melt, was used for the viscosity measurement. A platinum cylinder (OD 15 mm and the height of 20 mm) was used as the measuring corpus. Oscillations of the pendulum (inserted by servomotor) were registered by two phototransistors, placed in the path of a light beam reflected from a mirror connected to the pendulum. All measurements were performed in the temperature range of around 60 to 100 °C. When the whole sample was melted, the pendulum was immersed into the investigated melt, in such a way that the surface of the melt was always kept 2 mm over the top of the corpus of measuring cylinder. Deepness of the immersion was directed using a platinum electrical contact. The measuring device, including the temperature of the furnace, was directed by computer. After the input data and the necessary temperature profile were inserted, the measurement of viscosity was carried out automatically. An experimental error did not exceed 2.5 %. The measuring device and other aspects of the method are described in detail elsewhere [17].

2.4 Electrical Conductivity

A conductivity cell used for the experiments was based on a pBN capillary (Boralloy, Momentive™, U.S.A.) of 4 mm ID and 100 mm length. A platinum–rhodium alloy electrode (10 % of rhodium, rod 1 mm OD) was placed in a fixed position inside the pBN capillary. Vessel of the melted samples (made of the same alloy) worked as a counter electrode. A vessel containing ca 35 g of measured mixture was inserted into a closed vertical laboratory resistance furnace under an inert argon atmosphere with some overpressure. A Pt–Pt10Rh thermocouple was used for the temperature monitoring. An impedance/gain–phase analyzer (National Instruments™, a high–performance modular chassis controlled by Labview™ software) was used for the cell impedance measurement. Further experimental details of the procedure could be found elsewhere [18].

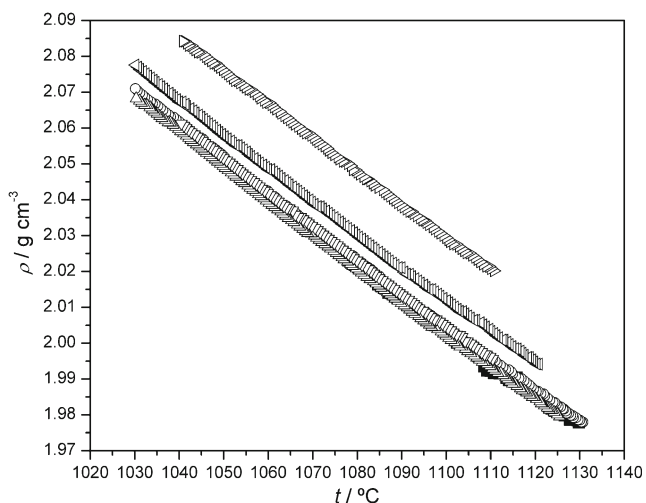


Fig. 1 Density (ρ) of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ as a function of temperature (t) for compositions: Na_3AlF_6 (■), 5 mole % SiO_2 (○), 10 mole % SiO_2 (Δ), 20 mole % SiO_2 (▽), 35 mole % SiO_2 (<), 50 mole % SiO_2 (>)

3 Results and Discussion

3.1 Density

Figure 1 shows the experimental data of density as a function of temperature and composition obtained in the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$. It could be seen that density varies linearly with temperature in all cases. Temperature dependence of the density could be formulated in the form of the linear equation

$$\rho = a + bt \tag{1}$$

where ρ is the density in $\text{g}\cdot\text{cm}^{-3}$, t is temperature in $^\circ\text{C}$, and a in $\text{g}\cdot\text{cm}^{-3}$, b in $\text{g}\cdot\text{cm}^{-3}\cdot^\circ\text{C}^{-1}$ are the coefficients of linear regression analysis.

Table 1 summarizes this linear regression together with the standard deviations. In Fig. 2, an isothermal dependence of the density on the concentration of SiO_2 is shown. As can be seen from the figure, the addition of SiO_2 into the melt only affects the density at high concentrations (35–50 mole

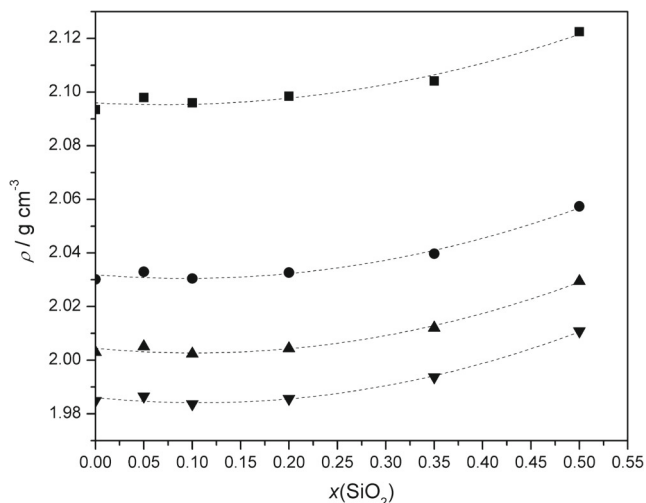


Fig. 2 Concentration dependences of density (ρ) of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ at: 1000 $^\circ\text{C}$ (■); 1070 $^\circ\text{C}$ (●); 1100 $^\circ\text{C}$ (▲); 1120 $^\circ\text{C}$ (▼)

% of SiO_2). This finding is in accordance with the work of Grjotheim et al. [6]. These authors reported that SiO_2 has no influence on the density of molten cryolite electrolytes with a low content of alumina.

The volume of two-component systems can be expressed as follows:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} dn_2 \tag{2}$$

where T is the thermodynamic temperature, P is the pressure and n_i is the amount of substances in the system. Partial derivations by amount of each substance (from Eq. 2) are partial molar volumes and are denoted \bar{V}_1 and \bar{V}_2 , where:

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} \tag{3}$$

The physical idea behind the concept of partial molar volume is the volume increase caused by the addition of 1 mole of component to the solution such that the composition of

Table 1 Density of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ as a function of temperature. Coefficients a and b in Eq. 1 and the standard deviation of approximations of the samples (SD)

$x_{\text{Na}_3\text{AlF}_6}$	x_{SiO_2}	$a/(\text{g}\cdot\text{cm}^{-3})$	$b \times 10^4/(\text{g}\cdot\text{cm}^{-3}\cdot^\circ\text{C}^{-1})$	$\text{SD}(a)/(\text{g}\cdot\text{cm}^{-3})$	$\text{SD}(b) \times 10^6/(\text{g}\cdot\text{cm}^{-3}\cdot^\circ\text{C}^{-1})$	$t/^\circ\text{C}$
1.00	0.00	2.99832	-9.04811	0.00653	5.92844	1060–1140
0.95	0.05	3.02659	-9.28606	0.00181	1.67654	1020–1130
0.90	0.10	3.03153	-9.35555	0.00182	1.68817	1020–1130
0.80	0.20	3.03863	-9.40174	0.00189	1.76222	1020–1130
0.65	0.35	3.02402	-9.19913	0.00179	1.66738	1020–1130
0.50	0.50	3.05318	-9.30661	0.00136	1.26614	1040–1130

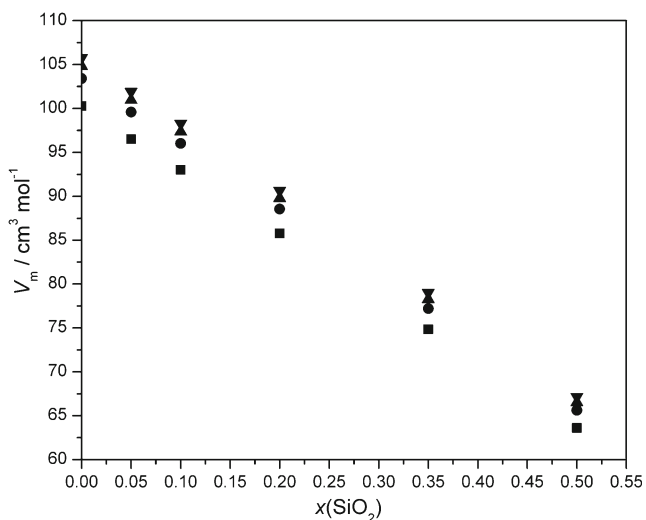


Fig. 3 Concentration dependences of molar volume (V_m) of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ at: 1000 °C (■); 1070 °C (●); 1100 °C (▲); 1120 °C (▼)

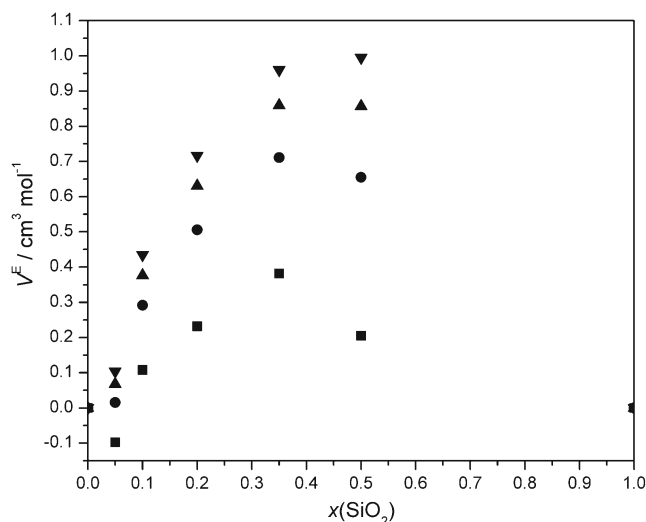


Fig. 4 Concentration dependences of excess molar volume (V^E) of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ at: 1000 °C (■); 1070 °C (●); 1100 °C (▲); 1120 °C (▼)

the solution at constant temperature and pressure does not change. A partial molar volume can thus reach a negative value, too. At the constant temperature and pressure and in one mole mixture ($dx_1 = dx_2$), the partial molar volume can be expressed as follows:

$$\bar{V}_2 = V_m + x_1 \left(\frac{\partial V_m}{\partial x_2} \right) \quad (4)$$

where V_m is the molar volume of the mixture. The molar volume of two-component systems can be obtained from the experimentally acquired density of the mixture (ρ_{exp}) and molar weights of each component (M_i):

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho_{\text{exp}}} \quad (5)$$

Composition dependence of molar volume (for different temperatures) of the investigated systems is depicted in Fig. 3. As can be seen, the molar volume of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ linearly decreases with the concentration of silica in the melt. Expression for the partial molar volume of SiO_2 in the molten system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ (in the form of second-order polynomial) could be found (for different temperatures) in Table 2. For the partial molar volume of SiO_2 in its infinitely diluted

solution ($x_{\text{SiO}_2} \rightarrow 0$) in the molten Na_3AlF_6 at the temperature of 1000 °C, the value of $\bar{V}_{\text{SiO}_2} = 28.81 \text{ cm}^3 \cdot \text{mol}^{-1}$ was acquired. This value is somewhat higher than that of a pure SiO_2 at these conditions ($V_{\text{SiO}_2}^* = 26.53 \text{ cm}^3 \cdot \text{mol}^{-1}$), calculated based on the density of tridymite [19]) which may relate to a little volume expansion after mixing. Table 2 contains parameters of the other volume relations in the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ (parameters of isotherms of molar volume, partial molar volume of silica and values of partial molar volumes of silica in infinitely diluted solutions of cryolite at different temperatures).

When comparing the molar volume of the melt and molar volume calculated according to additive model, the excess molar volume could be obtained:

$$V^E = V_m - V^{\text{id}} = V_m - \sum_i x_i V_i^* \quad (6)$$

where V_m is the molar volume, V_i^* is the molar volume of pure substance at the same condition, and V^{id} is the molar volume of investigated system calculated according to additive model ($\sum x_i V_i^*$). The excess molar volume is the volume that describes how much the real mixture deviated from the ideality (additive model), giving basic information

Table 2 Volume relations in the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$; x_1 , x_2 – mole fractions of Na_3AlF_6 and SiO_2 , respectively

$t/^\circ\text{C}$	$V_m/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\bar{V}_2/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\bar{V}_2/(x_1 \rightarrow 1; \text{cm}^3 \cdot \text{mol}^{-1})$
1000	$100.2 - 71.4x_2 - 3.4x_2^2$	$25.4 + 3.4x_1^2$	28.8
1070	$103.3 - 73.1x_2 - 4.6x_2^2$	$25.6 + 4.6x_1^2$	30.2
1100	$104.8 - 73.9x_2 - 5.1x_2^2$	$25.7 + 5.1x_1^2$	30.9
1120	$105.7 - 74.4x_2 - 5.5x_2^2$	$25.8 + 5.5x_1^2$	31.3

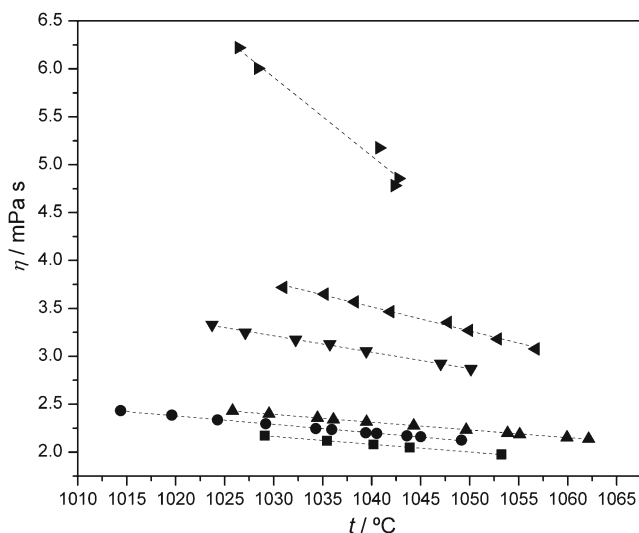


Fig. 5 Viscosity (η) of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ as a function of temperature (t) for compositions: Na_3AlF_6 (■); 5 mole % SiO_2 (●); 10 mole % SiO_2 (▲); 20 mole % SiO_2 (▼); 35 mole % SiO_2 (◄); 50 mole % SiO_2 (►)

about the chemical interactions inside the melt. Composition dependence of the excess molar volume of SiO_2 in the molten system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ can be seen in Fig. 4. The excess molar volume positively deviated from additive model ($V^E = 0$) almost in whole concentration range (5–50 mole % SiO_2). This deviation linearly increased in the concentration range from at least 5 mole % up to 35 mole %, where the trend of dependence is changing, indicating an alternation of the chemical interactions inside the melt at these concentrations.

3.2 Viscosity

Figure 5 shows experimental results of the viscosity measurement in the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$. These results are shown in the form of relationship between viscosity and temperature at the different concentrations of silica in molten cryolite. As can be seen, the viscosity of a pure cryolite, measured in this work, is in good agreement with the literature data [20, 21].

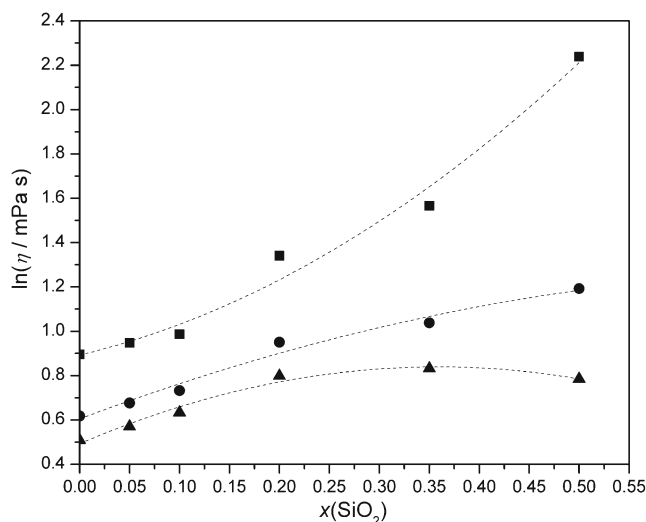


Fig. 6 Concentration dependences of logarithmic values of viscosity (η) of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ at: 1000 °C (■); 1070 °C (●); 1100 °C (▲)

A temperature dependence of viscosity is usually presented in the form of its logarithm:

$$\ln \eta = a + b/t \tag{7}$$

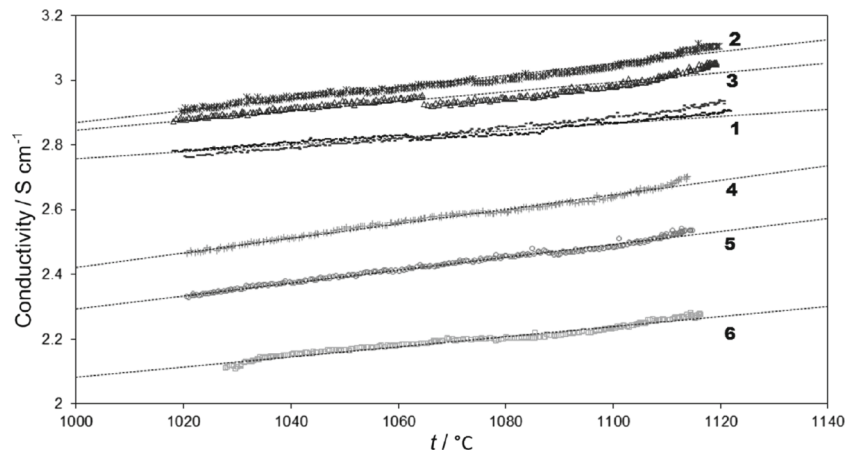
where η is the viscosity in mPa·s, t is the temperature in °C and a, b in °C are the coefficients of linear regression analysis. Values of the constants a and b earned by the linear regression together with the standard deviations are given in Table 3.

As can be seen from Fig. 5, the viscosity in all of the investigated mixtures varies linearly with the temperature. The slope of the temperature dependence is the same only in a small concentration range of silica (ca up to 10 mole % of SiO_2). At higher concentrations, the slope varies linearly with the concentration of silica in the molten cryolite. A small addition of silica to the molten cryolite (up to 10 mole %) could slightly increase viscosity, but has no influence on the slope of this dependence. Further addition of silica to the molten cryolite has, however, a huge effect on the viscosity, since it is responsible for a glassy-networks formation in the melt. Higher addition of silica also has the

Table 3 Logarithm of viscosity of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ as a function of temperature (Eq. 7), regression coefficients (a, b) and their standard deviations (SD) and measured temperature ranges (t) of the viscosity

$x_{\text{Na}_3\text{AlF}_6}$	x_{SiO_2}	a	$b/^\circ\text{C}$	SD(a)	SD(b)/ $^\circ\text{C}$	$t/^\circ\text{C}$
1.00	0.00	-3.3582	4254.3	0.0259	27.0	1020–1060
0.95	0.05	-3.2052	4153.3	0.0316	32.6	1010–1050
0.90	0.10	-2.8951	3881.6	0.0188	19.7	1020–1070
0.80	0.20	-4.6175	5957.9	0.1575	163.3	1020–1060
0.65	0.35	-6.4966	8062.3	0.3418	356.8	1020–1060
0.50	0.50	-13.7500	15988.6	1.5009	1555.0	1020–1050

Fig. 7 Electrical conductivity of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ as a function of temperature. Pure Na_3AlF_6 (1, -); 5 mole% SiO_2 (2, *); 10 mole% SiO_2 (3, Δ); 25 mole% SiO_2 (4, +); 35 mole% SiO_2 (5, o); 40 mole% SiO_2 (6, \square)



influence on the slope of the temperature dependence of viscosity.

Figure 6 shows a concentration dependence of logarithm of viscosity of the investigated system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$. As it can be seen from the figure, the logarithm of viscosity linearly increases up to ca 25 mole % of SiO_2 in the melt. Behind this concentration limit, the trends of this dependence differ across the isotherms. While for the lowest temperature (1000 °C), the logarithm of viscosity increases with the even higher slope than in the lower concentration range, for the isotherms of the higher temperature (1100 °C), the logarithm of viscosity, on the contrary, decreases with the concentration of silica in the melt.

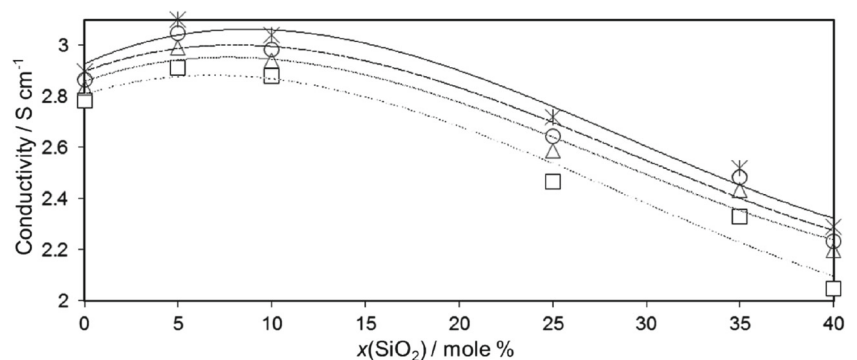
3.3 Electrical Conductivity

As can be seen in Fig. 7, conductivity in all of the investigated mixtures varied linearly with the temperature. Slope of the temperature dependence was the same for all mixtures. An addition of silica to the pure cryolite had, in general, a negative effect on the electrical conductivity of the cryolite melts, except for the lower concentrations of silica (5 and 10 mole %).

Conductivity of the investigated systems as a function of the content of SiO_2 is shown in Fig. 8. As can be seen from

the figure, the isothermal dependency can be divided into two parts. The first one represents the region up to 10 mole % of SiO_2 , the second one represents the region with composition from 10 mole % to 40 mole % (and probably more) of SiO_2 . While the conductivity considerably decreases with concentration of SiO_2 in the second part (in agreement with previous works [7, 14, 15]), it surprisingly slightly rises with the concentration in low concentration of SiO_2 . This trend of conductivity isotherms (at small concentrations of SiO_2) is not in agreement with the previous works [7, 14, 15]. Conductivity of a pure cryolite as well as the conductivity values of $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ mixtures mostly differs from the values measured by Belyaev [14] and Sokhanvaran et al. [15]. In general, a deviation in certain values of the conductivity is in the case of Grjotheim et al. [7] up to ca 6 %, in the case of Belyaev [14] up to ca 20 %, and in the case of Sokhanvaran et al. [15] up to ca 20 %. Detailed discussion on the topic could be found elsewhere [18]. However, it can be concluded, that the electrical conductivity decreases with an increasing concentration of silica in the molten cryolite, since a high content of silica is responsible for a glassy-networks raise in the melt and is accompanied by a substantial increase of viscosity (Fig. 5) and thus degradation of the transport properties and conductivity (see Fig. 7 and Fig. 8).

Fig. 8 Conductivity isotherms of the system $\text{Na}_3\text{AlF}_6\text{-SiO}_2$: 1000 °C (\square); 1070 °C (Δ); 1100 °C (o); 1120 °C (*)



4 Conclusions

Density, viscosity and electrical conductivity of the molten system $\text{Na}_3\text{AlF}_6\text{--SiO}_2$ have been investigated in the concentration range up to 50 mole % of SiO_2 . The partial molar volume of SiO_2 in its infinitely diluted solution in the molten Na_3AlF_6 is $\overline{V}_{\text{SiO}_2} = 28.81 \text{ cm}^3 \cdot \text{mol}^{-1}$. This value is slightly higher than that of a pure SiO_2 ($V_{\text{SiO}_2}^* = 26.53 \text{ cm}^3 \cdot \text{mol}^{-1}$) which relates to volume expansion after mixing. The excess molar volume of SiO_2 positively deviated from additive model. This deviation linearly increased in the concentration range from ca 5 mole % up to 35 mole %, where the trend of dependence is changing. The viscosity in all of the investigated mixtures varies linearly with the temperature. A small addition of silica to the molten cryolite (up to 10 mole %) slightly increases viscosity. Further addition of silica to the molten cryolite has, however, a huge effect on the viscosity, since it is responsible for a glassy–networks formation in the melt. This observation is also supported by results from the electrical conductivity measurement. A high content of silica is responsible for a glassy–networks raise in the melt and is accompanied by a substantial increase of viscosity and degradation of the transport properties like conductivity.

Acknowledgments This work was supported by the Science and Technology Assistance Agency (APVV-0460-10 and SK-CN-0029-12), and by the Slovak Grant Agency (VEGA 2/0179/10 and VEGA 2/0095/12). The authors also want to acknowledge the China-Slovakia Inter–governmental S&T Cooperation Program. This publication is the result of the project implementation: “Applied research of technology of thermal plasma processes”, ITMS code 26240220070, supported by the Research & Development Operational Program funded by the ERDF.

References

- Istratov AA, Buonassisi T, Pickett MD, Heuer M, Weber ER (2006) Control of metal impurities in “dirty” multicrystalline silicon for solar cells. *Mater Sci Eng B* 134:282–286
- Bieber AL, Massot L, Gibilaro M, Cassayre L, Taxil P, Chamelot P (2012) Silicon electrodeposition in molten fluorides. *Electrochim Acta* 62:282–289
- Boen R, Bouteillon J (1983) The electrodeposition of silicon in fluoride melts. *J Appl Electrochem* 13:277–288
- Elwell D, Feigelson RS Electrodeposition of solar silicon. *Sol Energy Mater Sol Cells* 6:123–145
- Elwell D, Rao GM (1988) Electrolytic production of silicon. *J Appl Electrochem* 18:15–22
- Grjotheim K, Matiašovsky K, Fellner P (1982) The electrodeposition of silicon from cryolite melts. *Light Met*:333–341
- Grjotheim K, Matiašovsky K, Fellner P, Silný A (1971) Electrolytic deposition of silicon and silicon alloy. *Can Metall Q* 10:79–82
- Monnier R, Barakat D (1965) Dual cell refining of silicon and germanium. US Patent 3,219,561,
- Monnier R, Barakat D, Giacometti JC (1966) Refining of silicon and germanium. US Patent 3,254,010,
- Monnier R, Giacometti JC (1964) Recherches sur le raffinage électrolytique du silicium. *Helv Chim Acta* 47:345–353
- Oishi T, Watanabe M, Koyma K, Tanaka M, Saegusa K (2011) Process for solar silicon production by molten salt electrolysis using aluminium-silicon liquid alloy. *J Electrochem Soc* 158:E93–E99
- Olsen KS, Martinez AM, Rolseth S, Gundbransen H, Juel M, Haarberg GM (2010) Electrodeposition of crystalline silicon films from alkali fluoride mixtures. *Electrochem Soc Trans* 33:429–438
- Olson JM, Carleton KL (1981) A semipermeable anode for silicon electrorefining. *J Electrochem Soc* 128:2698–2699
- Belyaev AI (1947) Physicochemical processes at electrolysis of aluminium. Metallurgizdat, Moscow
- Sokhanvaran S, Thomas S, Barati M (2012) Charge transport properties of cryolite-silica melts. *Electrochim Acta* 66:239–244
- Weil DF, Fyfe WJ (1964) The 1010 and 800 °C isothermal section in the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{O}_3\text{--SiO}_2$. *J Electrochem Soc* 111:582–585
- Daněk V (2006) Physicochemical analysis of molten electrolytes. Elsevier
- Korenko M, Priscak J, Šimko F (2013) Electrical conductivity of systems based on $\text{Na}_3\text{AlF}_6\text{--SiO}_2$ melt. *Chem Pap*:1350–1354
- Physical constants of inorganic compounds (2005) In: CRC Handbook of chemistry and physics. CRC Press, Boca Raton
- Brockner W, Tørklep K, Øye HA (1979) Viscosity of sodium fluoride-aluminium fluoride melt mixtures. *Ber Bunsenges Phys Chem* 83:12–19
- Robelin C, Chartrand P (2011) A viscosity model for the $(\text{NaF}+\text{AlF}_3+\text{CaF}_2+\text{Al}_2\text{O}_3)$ electrolyte. *J Chem Thermodyn* 13:761–771