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Thermal analysis of the Na_2O-rich concentration region of the quasi-binary system $Na_2O–SiO_2$

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ABSTRACT

The phase diagram of the Na_2O-rich concentration region of the binary system $Na_2O–SiO_2$ was derived from STA measurements. The eutectic was established at about 1134 ± 9 K between 78 and 80 mole per cent of sodium oxide. The XRD measurements showed the existence of a crystal structure which was unknown so far. Its composition is most likely $Na_{10}SiO_7$ which was also deducted from the shape of the liquidus line obtained for all samples measured in the high Na_2O concentration range of the binary system $Na_2O–SiO_2$. A second eutectic is placed between 85 and 87 mole per cent of sodium oxide at 1118 ± 15 K. The structure change of Na_2O ($\beta \rightarrow \alpha$) should take place at 1243 K but was not observed in any sample in the Na_2O-rich concentration region of the binary system $Na_2O–SiO_2$.

1. Introduction

The quasi-binary system $Na_2O–SiO_2$ is the basis for an understanding of the behaviour of one important oxide system relevant to fuel ashes and slags. The knowledge of the complete quasi-binary phase diagram of more complex systems, like quaternary or even higher component systems, which are closer to the real systems existing in processes like coal combustion and gasification, is essential. Sodium silicates are also a part of numerous minerals, so that the thermodynamic properties of the $Na_2O–SiO_2$ system are of great interest for various branches of earth science and are important for the development of new technologies in metallurgy or in production of glass and ceramics [1].

Many groups [2–10] contributed to the investigation of the thermodynamic properties in the $Na_2O–SiO_2$ system. The first information about the binary system sodium metasilicate–silicon oxide can be found in Morey and Bowen's work [2]. Only one compound, sodium disilicate, exists between sodium metasilicate and silica. The melting point of Na_2SiO_3 was found at 1088 °C. The eutectic between Na_2SiO_3 and $Na_2Si_2O_5$ is placed at 840 °C, 68.75 mole per cent SiO_2. $Na_2Si_2O_5$ (sodium disilicate) melts congruently at 874 °C. The second eutectic point, between the disilicate and quartz, was determined at 793 °C and 82.5 mole per cent SiO_2. The melting point of cristobalite was determined at 1710 °C. Kracek [4,5] extended the investigation and included the sodium orthosilicate. In the field between Na_2SiO_3 and SiO_2 the phase diagram was in agreement with previous work [2]. The eutectic between sodium orthosilicate and the metasilicate is placed at 1022 °C and 43.8 mole per cent SiO_2. In the case of sodium orthosilicate, Na_4SiO_4, the liquidus raises steeply from the eutectic to 1118 ± 5 °C at 41.3 mole per cent SiO_2. Above this temperature the orthosilicate is unstable and it decomposes into liquid and Na_2O crystals. A new compound, $Na_6Si_8O_{19}$, was reported by Williamson and Glaser [6]. It melts incongruently to SiO_2 and liquid at 808 ± 2 °C and it disproportionates to β-$Na_2Si_2O_5$ and quartz at 700 ± 10 °C. In the range between $Na_4SiO_4–Na_2SiO_3$ a new compound, $Na_6Si_2O_7$, has been described by Loeffler and D'Ans [8,9]. The phase diagram in the range between pure Na_2O and Na_4SiO_4 was mainly estimated [1,8–10]. The authors [8,9] compared their own data with data from Zintl, Morawietz (according to [8]) and Bunzel, Kohlmeyer [11]. They assumed that, if the sodium oxide is molten at 925 °C [11] and there is no intermediate phase between Na_2O and Na_4SiO_4, it is expected that the eutectic point in the high sodium oxide range is at 92.5 mole per cent Na_2O and 800 °C. Na_4SiO_4 exists in two forms and phase transformation takes place at 960 °C and from 66.66 to 71 mole per cent Na_2O (β-Na_4SiO_4). The α-form melts congruently at 1078 °C. The eutectic point between Na_4SiO_4 and $Na_6Si_2O_7$ is at 962 °C and 63.5 mole per cent Na_2O. $Na_6Si_2O_7$ has its congruent melting point at 1115 °C. Another eutectic point is placed in the range between $Na_6Si_2O_7$ and Na_2SiO_3 at 1015 °C and 54.5 mole per cent Na_2O; Na_2SiO_3 melts at 1088 °C. It can be also seen that $Na_6Si_2O_7$ exists only up to 402 °C [8].

In Zaitsev et al.'s studies [1,10] the properties of the $Na_2O–SiO_2$ system were studied by Knudsen effusion mass spectrometry in

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the range 19.5–61.8 mole per cent Na_2O. The activities of the constituent oxides were determined. In these studies a thermodynamic model for Na_2O–SiO_2 melts was proposed and used to calculate phase equilibrium in the system. The results of the calculation agree well with the experimental data obtained by physicochemical methods by Kracek and others. The authors suggested in the Na_2O-rich concentration part of the phase diagram one eutectic at 930 °C and $x(SiO_2) = 0.267$. Also two structure changes of Na_2O at 750 and 970 °C were expected.

By using thermodynamic modelling the known equilibrium information can be extended to uninvestigated equilibrium or a metastable region. Therefore, the phase equilibrium in the whole range of phase diagram was calculated by Yazhenskikh as well [12,13] by using the associate model for the liquid phase. A quite good agreement of the calculation performed using the optimized data set with experimental data was observed. As a result of this calculation, in the high Na_2O concentration part of the system, one should observe a simple eutectic existing at about 78 mole per cent Na_2O and at about 937 °C. The calculation in the range $x(SiO_2) = 0.33$–1.0 were done by Wu et al. [14], Chartrand and Pelton [15] and Romero-Serano et al. [16]. All available thermodynamic and phase equilibrium data for this system were simultaneously critically evaluated in order to obtain one set of model equations. The calculated phase diagram [14] reproduces very well the measured one. Small disagreements were observed in the places which were usually extrapolated by authors who used physicochemical methods, which can be the reason of such differences. Chartrand and Pelton [15] have used the modified quasichemical model. Experimental activities in the liquid were closely reproduced in this work. Romero-Serrano et al. [16] used a structural model for the silicate melts and glasses and a least-squares optimization method for the liquid phase to calculate the thermodynamic properties and phase diagram for this binary system. This optimized phase diagram was based on the phase diagram reported by Kracek, D'Ans, Loeffler and Williamson et al. and from activities of Na_2O and SiO_2 in the liquid estimated by the electromotive force technique or/and chemical equilibration method. Some of the data were also taken from JANAF tables. Some changes in comparison with previous work [14] could be seen in the range $x(SiO_2) = 0.33$–0.50 in case of temperature of eutectics 1001 and 996 °C (previous [14] 1031 and 1016 °C, respectively).

The information about pure Na_2O is rather avaricious [11,17]. Bouaziz and Papin investigated Na_2O in some binary systems with NaOH, Na_2CO_3 and Li_2O [18–20]. They proposed the melting point of Na_2O at 1132 °C and the structure transformations $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ at 750 °C and 970 °C, respectively.

2. Experimental

In previous works [2,4,5] samples were produced by "carbonate synthesis". Sodium carbonate was used in the whole known range of the phase diagram to produce Na_2O/SiO_2 mixtures. The Na_2O is formed in situ by decomposition of Na_2CO_3 during reaction with SiO_2 in this preparation route. Kracek [4,5] observed that the preparations have a tendency to retain CO_2 with increasing Na_2O/SiO_2 ratio. Therefore, the best way to produce samples in the part of the systems where sodium oxide is in excess was using pure sodium oxide for preparation. Since the commercially available Na_2O has a purity of 87% (Alfa) and 81% (Aldrich), pure Na_2O had to be synthesised for the present investigation.

Different ways of production of sodium oxide are available in the literature [21–24]. The method of Zintl and Baumbach [24] was chosen to produce Na_2O. It was a little modified after a few first syntheses have been done. The sodium oxide was produced inside a stainless steel tube under vacuum in a nickel vessel. NaN_3 (Merck, extra pure) and $NaNO_3$ (Aldrich, nominal purity 99.99%) were mixed under argon in the required proportions with a small addition of sodium azide, which is important to protect formed Na_2O from oxidation:

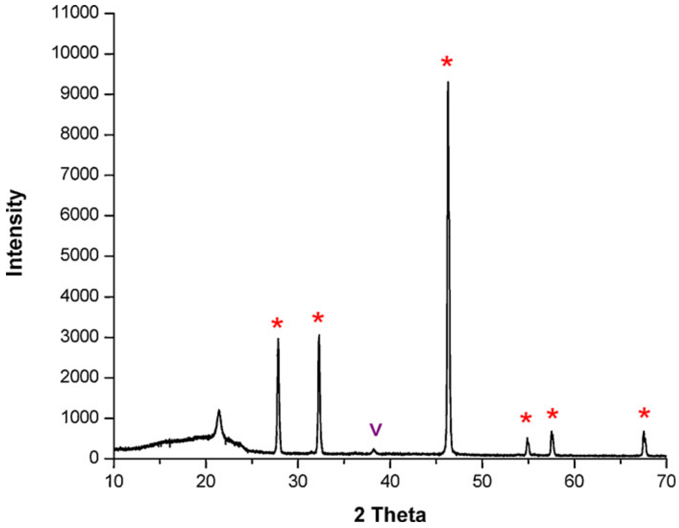

Fig. 1. XRD pattern of sodium oxide after preparation (the peak at about 20° originates from the foil, which protects the sample). * Na_2O; v NaOH.

$$5(1/2)NaN_3 + NaNO_3 \rightarrow 3Na_2O + 8(3/4)N_2 + (1/2)Na \qquad (1)$$

The mixture was dried at 493 K for about 8 h. Then the temperature was slowly (0.5 K/min) increased up to 643 K where the main reaction took place and kept for about 10 h. The sodium azide reacted with sodium nitrate and a high amount of gaseous nitrogen was released. After this part of the synthesis the temperature was slowly increased up to 693 K (about 0.2 K/min) and the rest of the metallic sodium was distilled (1.5–2 h). After reaction the tube was cooled down to room temperature and opened under protective argon atmosphere. The phase composition of the product was characterized using XRD (Fig. 1). A very weak XRD signal of NaOH could be observed. A repetition of the XRD measurement after 20 min has shown that reflexes from sodium hydroxide increase with time. Na_2O reacted with water from air and NaOH was formed during the XRD measurement.

All chemicals were handled in a high purity argon atmosphere (water content <1 ppm). Mixtures of Na_2O and SiO_2 (Alfa, nominal purity 99.9%), in appropriate proportions (listed in Table 1), were melted in vacuum-sealed platinum ampoules, homogenised and solidified. After preparation the samples were ground to finest powder in an agate mortar. X-ray diffraction measurements were done to verify the preparation of the binary compositions (as an example – Fig. 2). All samples in the Na_2O-rich concentration region were composed of Na_2O and Na_4SiO_4 as it was estimated in Refs. [1,8–10,12,13]. A very weak XRD signal of NaOH could be observed, which is formed in reaction of Na_2O with moisture from air during XRD measurements. The homogenous mixtures of different composition were examined by means of combined DTA/TG analysis. Samples of 120–200 mg were filled in platinum ampoules (about 5 mm diameter, 15–20 mm length). Experiments were conducted at heating and cooling rates ranging between 5 and 1 K min^{-1} and for better protection the samples were measured under vacuum (10^{-4} mbar). A Simultaneous Thermal Analyser, type STA 429, supplied by Netzsch (Selb, Germany) was used in this study. The heating as well as the cooling schedules for the samples were programmed using the software provided by Netzsch and measurements were automatically recorded. The software package also included mathematical profiles for peak separation to resolve over-

Table 1
Results of the DTA experiments in the quasi-binary system Na_2O–SiO_2 (up – thermal effects during heating, down – thermal events during cooling). For Na_2O the probable error was calculated – it is given in per cent. It is based on the observation of the mass loss during annealing.

Sample	Molar ratio of Na_2O (%)(error (%))	Thermal effects (K)											
		T1 structure change of Na_2O		T2		T3 eutectic_1		T4 eutectic_2		T5 structure change of Na_4SiO_4		T6 liquidus	
		Up	Down	Up	Down	Up	Down	Up	Down	Up	Down	Up	Down
0.96	95.98 (0.1)	1023	1020	1068	1053	–	–	–	–	–	–	1353	1307
0.92	91.96 (0.4)	1024	1018	–	–	1115	1113	–	–	–	–	1288	1244
0.90	89.98 (0.2)	1025	1019	–	–	1126	1125	–	–	–	–	1246	–
0.87	87.16 (0.5)	1023	1018	–	–	1099	1110	–	–	–	–	1184	1169
0.85	84.90 (0.3)	1020	1020	–	1085	1132	1140	–	–	–	–	[a]	[a]
0.83	83.53 (0.4)	1019	1026	1053	1073	–	–	1122	1127	–	–	1245	1165
0.82	81.97 (0.1)	1021	1015	–	–	–	–	1126	1131	–	–	1212	1184
0.80	79.98 (0.4)	1024	1020	–	1089	–	–	1138	1139	–	–	1173	1159
0.78	77.89 (0.2)	1020	1016	–	1076	–	–	1139	1136	–	–	–	–
0.76	75.98 (0.6)	1024	1018	–	–	–	–	1098	1114	–	–	1210	1201
0.735	73.50 (0.1)	–	–	–	–	–	–	1151	1152	1235	1227	1243	1230
0.72	71.98 (0.3)	–	1015	–	–	–	–	1130	1126	1231	1223	1284	1264
0.70	69.98 (0.2)	1023	1021	–	–	–	–	1130	1110	1230	1226	1347	1324
0.68	67.95 (0.1)	–	–	–	–	–	–	–	–	1229	1223	1362	1314
0.67	66.93 (0.3)	–	–	–	–	–	–	–	–	1233	1225	1363	1300
0.63	63.01 (0.2)	–	–	1302[b]	–	–	–	–	–	1231	1222	1343	1234

[a] Samples were measured up to 1223 K.

[b] Temperature of eutectic in range $0.6 < x(Na_2O) < 0.6667$).

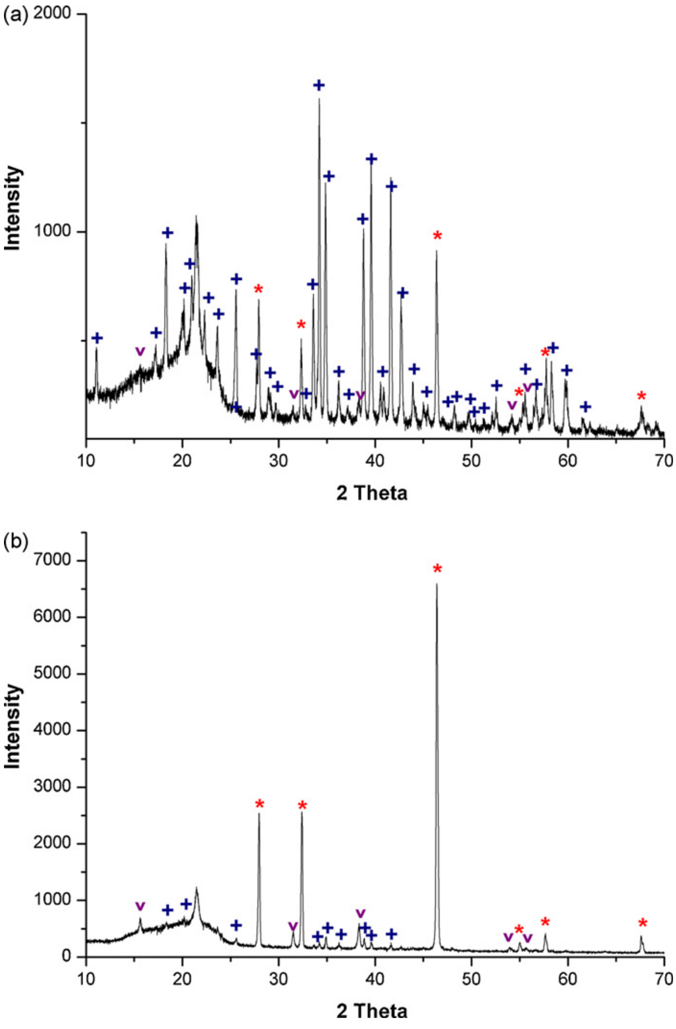

Fig. 2. XRD patterns of the samples $x(Na_2O) = 0.72$ (a) and $x(Na_2O) = 0.96$ (b) after preparation. * Na_2O; v NaOH; + Na_4SiO_4.

lapping peaks of DTA curves. Temperatures were measured with Pt/(Pt + 10%Rh) thermocouples. The thermocouples were calibrated using the structure change or melting temperatures of well known substances recommended by ICTA (Standard Reference Material 760). The accuracy of the observed thermal effects was estimated as ±10 K.

3. Results and discussion

The Na_2O-rich concentration region of the Na_2O–SiO_2 system was established for the first time in the present work. Some characteristic heating and cooling thermograms (heating rate 5 K min^{-1}) are exemplified in Fig. 3 and they correspond to the samples with compositions $x = 0.72$, 0.78, 0.80, 0.83, 0.87, 0.90 and 0.96, respectively, where x denotes the mole fraction of Na_2O.

In case of melting temperature or solidification temperature the difference between the thermal effects observed upon heating and cooling is caused by supercooling, therefore heating curves were analysed to compile temperature data. During all STA measurements no or insignificant mass losses were observed.

The following general remarks were made in the DTA measurements:

a. Samples with $x(Na_2O)$ values between 0.6667 and 0.76 show, in general, three thermal arrests (Fig. 3a):
   - the first effect at above 1235 K corresponds to the liquidus temperature, which value decrease with increasing sodium oxide content;
   - the effect at 1230 K can be ascribed to the structure change of Na_4SiO_4. Na_4SiO_4 exists in two forms. The phase transformation between β-Na_4SiO_4 and α-form takes place at 1233 K [8,9];
   - and the third one at about 1130 K – can be undoubtedly ascribed to the eutectic.

   Some of the samples (Table 1) show also a thermal effect at 1023 K, which can be identified as a structure change of sodium oxide reported by Bouaziz et al. [18].

   Exceptions are the sample 0.68 and 0.67, where only liquidus temperature and structure change of Na_4SiO_4 were observed (Table 1).

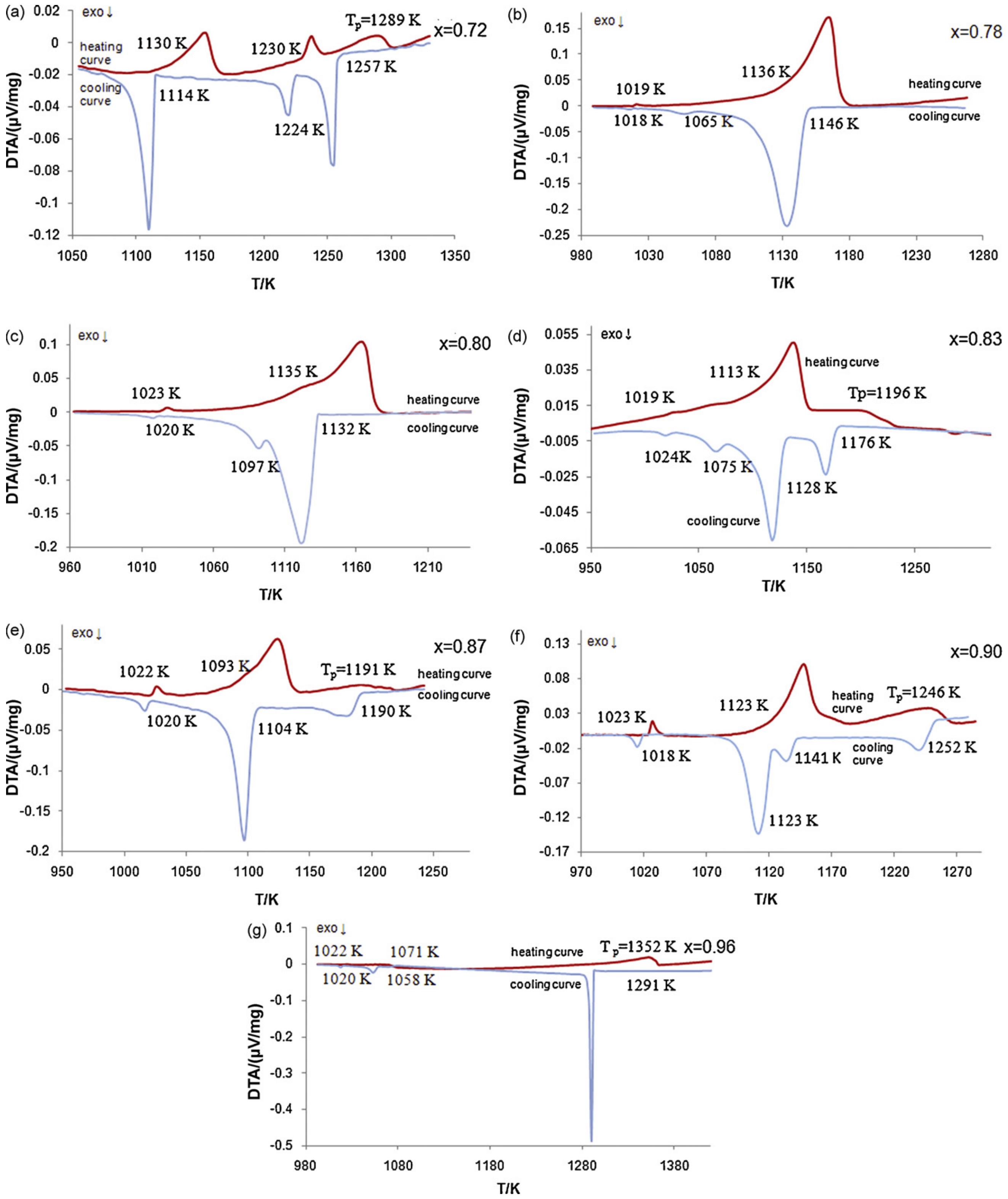

Fig. 3. DTA heating and cooling curves for Na_2O–SiO_2 mixtures of different composition: $x(Na_2O) = 0.72$ (a), 0.78 (b), 0.80 (c), 0.83 (d), 0.87 (e), 0.90 (f), 0.96 (g) (heating rate 5 K min^{-1}). All temperatures specified in figures are onset temperatures, otherwise it is written (T_p – peak temperature).

b. The thermograms obtained for mixtures with composition $x(Na_2O) = 0.78$ indicate two endothermic peaks (Fig. 3b): one at 1019 K corresponds to the solid–solid transition of sodium oxide $\gamma \rightarrow \beta$ [18]. The other, quite wide, strong peak at 1136 K – can be ascribed to the eutectic.

c. In the composition range $0.80 \leq x(Na_2O) \leq 0.83$, in general, three thermal effects are present in thermograms (Fig. 3c and d). Two of them – at about 1021 K and about 1131 K correspond to the structure change of Na_2O and the eutectic, respectively. The third one corresponds to the liq-

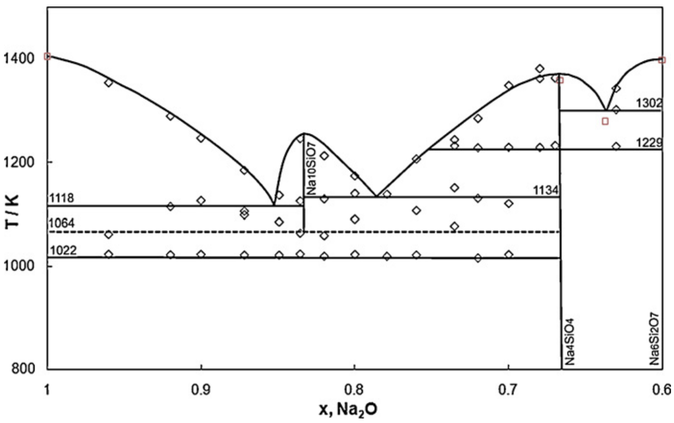

Fig. 4. Thermal effects detected for the Na_2O–SiO_2 mixtures and phase diagram of the high Na_2O concentration part of the Na_2O–SiO_2 system. □ – data from Bouaziz et al. [18] for pure Na_2O and from Zaitsev et al. [1,10] in range $x(Na_2O) = 0.6$–0.6667.

uidus temperature and is different for different samples (Table 1).

d. For the mixture of the composition $x(Na_2O) = 0.85$ two thermal effects at 1020 and 1132 K are observed, which can be ascribed to the structure change of sodium oxide and the eutectic, respectively. The sample was measured only up to 1223 K and no other arrest was observed (Table 1).
e. A strongly shifted temperature of the eutectic (at about 1093 K), liquidus at 1191 K and thermal arrest of the structure change of Na_2O at 1022 K appear in the sample with the composition $x(Na_2O) = 0.87$ (Fig. 3e)
f. The mixtures of the composition $x(Na_2O) = 0.90$ and 0.92 (Fig. 3f and Table 1, respectively) show three thermal effects: the liquidus, which temperature increases with increasing content of sodium oxide; a thermal arrest corresponds to the eutectic at about 1120 K, and the structure change of Na_2O $\gamma \rightarrow \beta$ at 1023 K.
g. A thermal event at 1352 K, which corresponds to the liquidus temperature, and the structure change of γ-Na_2O into β-Na_2O at 1022 K appear in the sample with composition $x(Na_2O) = 0.96$ (Fig. 3g).
h. The origin of the additional and weak thermal effect, observed in STA thermograms at about 1073K for the mixtures of the composition $x(Na_2O) = 0.96$, 0.85, 0.83, 0.80, 0.78 remains so far unnamed. The effect is more visible during cooling than during heating.

The proposed diagram of the high Na_2O concentration part of the Na_2O–SiO_2 system in the temperature range of 800–1500 K presented in Fig. 4 explains the thermal effects identified in the DTA curves and the results of the XRD measurements (as an example, Fig. 2 – after preparation; 5 – after STA measurements). Table 1 gives the average values of the thermal effects obtained from several cooling and heating segments for each sample. The temperatures obtained during heating were included in the table as an "up" thermal effect; the effects obtained during cooling were included in the table as a "down" thermal effect. For the determination of the eutectic temperature the average of the different measurements and the standard deviation are calculated.

Some comments should be made. The shape of the liquidus line shows that two eutectics should exist in the Na_2O-rich part of the Na_2O–SiO_2 system, one between 78 and 80 mole per cent of sodium oxide and rather closer to 78 mole per cent of Na_2O, because in some measurements of sample $x(Na_2O) = 0.78$ a small hill has been placed just before the eutectic peak on cooling, which suggests that with small changing of composition, the liquidus appears. The second eutectic in the Na_2O-rich concentration part of the binary system is placed between 85 and 87 mole per cent Na_2O. In Fig. 3e one can observe thermal events of the sample $x(Na_2O) = 0.87$. A well defined liquidus temperature is observed at 1191 K. Then a wide peak is seen at about 1093 K. It is quite well reproducible on cooling at 1104 K. Although the temperature is lower than the usually observed eutectic the peak is identified as an eutectic. This decrease of temperature could be caused by the width of peak. In this case it was rather difficult to define the onset of temperature. For the mixture of the composition $x(Na_2O) = 0.85$ the eutectic temperature was observed higher than for the other samples in this range (Table 1). The most probable explanation of such discrepancy is a small amount of liquid phase (sample is located nearby the eutectic point), presented in the sample, which subtly increases the thermal effect of the eutectic temperature.

If two eutectics exist between Na_2O and Na_4SiO_4 ($1 \leq x(Na_2O) \leq 0.6667$) a compound should exist in between. The previously unknown compound is most likely $Na_{10}SiO_7$, which melts congruently at about 1243 K. However, there is some uncertainty as to the temperature range in which it is stable. The Gibb's rule excludes in the equilibrium state of a binary system the existence of three components. If the thermal arrest at 1064 K (Fig. 4) is the temperature of decomposition of the new phase into Na_2O and Na_4SiO_4 and the kinetic of this process is slow it is possible to see the crystals of the new phase in the XRD diagrams of the measured samples even at low temperatures (Fig. 5, ?

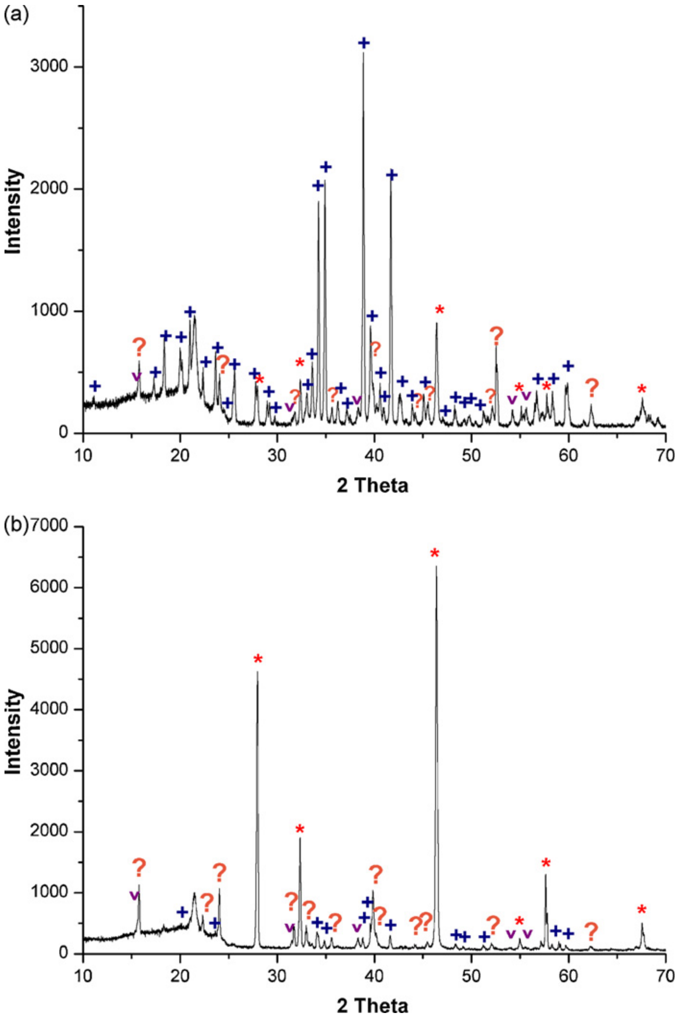

Fig. 5. XRD patterns of the samples $x(Na_2O) = 0.72$ (a) and $x(Na_2O) = 0.96$ (b) after STA measurements. * Na_2O; v NaOH; + Na_4SiO_4; ? unknown phase.

unknown phase). Therefore, the $Na_{10}SiO_7$ exists most likely at lower temperature as a metastable phase.

The sample with $x(Na_2O) = 0.83$ (Table 1, Fig. 3d) has its eutectic temperature placed in between both eutectics exist in the Na_2O-rich concentration range of the phase diagram. In this case it is not sure if the composition of this sample was smaller or higher than the composition of the pure compound ($Na_{10}SiO_7$). A small change of composition places the sample in another part of the phase diagram. Also overlapping of peaks could cause such situation. Therefore, the discrepancy of the eutectic temperature could be observed.

The STA measurements done on pure Na_2O have shown the phase transition of NaOH – β-phase to α-phase – at about 563 K according to [18]. The discontinuities of DTA curve at about 1016 K can be ascribed to the structure change of sodium oxide. Up to 1273 K the mass loss was insignificant. At about 1273 K a sudden mass loss and discontinuities of DTA curve were observed. At this temperature it looks like the sodium oxide decomposes. If the partial pressure of O_2 is low enough (measurements were done in vacuum), it is possible to reduce sodium oxide into metallic sodium which vaporizes at the temperature of the measurement. In addition, experiments with commercial Na_2O (Aldrich) were done. The purity of this sodium oxide was 81.41%, the rest of the chemical was Na_2O_2, NaOH, Na_2CO_3. A thermal arrest at about 560 K, an exothermic peak at about 750 K (more likely Na_2O_2 decomposition) and sudden mass loss connected with DTA signal discontinuities at about 1020 K and an endothermic peak at 1397 K were observed. Although the melting point of sodium oxide was not established in pure Na_2O in this work, it is more likely 1405 K as given by Bouaziz et al. [18] than at 1203 K given by Bunzel and Kohlmeyer [11] and used in the work of Loeffler [8]. It was concluded from measurements which were done for the mixture with composition $x(Na_2O) = 0.96$ (see Fig. 3g) and the commercial sodium oxide. For this mixture ($x(Na_2O) = 0.96$) the effect at 1352 K could be undoubtedly ascribed to the liquidus temperature. The eutectic temperature for this sample was not observed. A similar situation can be observed on the opposite side. For samples with $x(Na_2O) = 0.67$ and 0.68 the eutectic temperature was also not observed (Table 1). A likely explanation of this behaviour can be the small amount of the phase undergoing the eutectic transformation what is in agreement with level rule. Another explanation can be a slight solubility of $Na_{10}SiO_7$ in Na_2O or/and in Na_4SiO_4.

In Fig. 3g the structure change of Na_2O ($\gamma \rightarrow \beta$) can be observed at about 1023 K (heating curve). The intensity of the peak at about 1023 K increases with increasing sodium oxide content. From observation done by Bouaziz et al. [18] it is known that another structure transition ($\beta \rightarrow \alpha$) should take place at 1243 K which is neither observed in this measurement nor in another one. The authors suggested that the amount of energy which is absorbed or released during this transformation is four times smaller than that of the melting point of Na_2O. On the other hand the heat transition of the structure change at 1023 K is 25 to 30 times smaller and anyway this transformation is observed in Fig. 3g or f. Therefore, it seems that this structure does not exist.

In the range of the binary Na_2O–SiO_2 system, where the phase equilibrium were previously investigated by Kracek [4,5] and D'Ans and Loeffler [8,9] ($x(Na_2O) = 0.6$–0.666) also one sample was measured (Fig. 4) and a generally good agreement between previous data [8,9] or calculations [1,10] and experiments done in this work was observed. The few K difference of eutectic temperature between Na_4SiO_4 and $Na_6Si_2O_7$ can be explained by the other method of detecting the thermal events in the system and the volatility of one compound. The experimental phase diagram of the Na_2O–SiO_2 system in range $x(Na_2O) = 0.6667$–1 not really agrees with those calculated phase diagrams in Refs. [1,8–10,12,13] were only one simple eutectic was predicted.

4. Conclusions

For the quasi-binary system Na_2O–SiO_2 the most important part of this work was finding a suitable method of preparing the samples and making the measurements since one component – sodium oxide – is hygroscopic and volatile. A simultaneous thermal analyser was used to study the thermal effects of the Na_2O-rich concentration region of the quasi-binary system Na_2O–SiO_2 in the range of 300–1450 K. X-ray diffraction analyses of the samples were performed for phase identification. For the first time a new eutectic was established at about 1134 ± 9 K between 78 and 80 mole per cent of sodium oxide. The existence of a crystal structure with most likely composition $Na_{10}SiO_7$, which was unknown so far, was anticipated. A second eutectic is placed between 85 and 87 mole per cent of sodium oxide at a temperature of 1118 ± 15 K. The structure change of Na_2O ($\beta \rightarrow \alpha$) at 1243 K [18–20] was not observed in any sample in the high Na_2O range of the Na_2O–SiO_2 system.

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