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Low-temperature synthesized aluminosilicate glasses

Part III *Influence of the composition of the silicate solution on production, structure and properties*

H. RAHIER, W. SIMONS, B. VAN MELE*
Department of Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium

M. BIESEMANS
High Resolution NMR Centre, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium

The low-temperature reaction between an aqueous sodium or potassium silicate solution and metakaolinite yields a solid aluminosilicate. The influence of the molar ratios H_2O/R_2O (between 6.6 and 21.0) and SiO_2/R_2O (between 0.0 and 2.3) of the silicate solution (R = Na or K) on the aluminosilicate's production, on the reaction stoichiometry and on the aluminosilicate's molecular structure is studied with differential scanning calorimetry, ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR), cross-polarization MAS NMR, Fourier transform infrared spectroscopy and X-ray diffractometry. The reaction stoichiometry is determined by a one to one ratio for R/Al. H_2O/R_2O has no influence on the molecular structure of the aluminosilicate. Aluminium in the aluminosilicate is four-fold coordinated for the whole range of silicate solutions investigated. Moreover, Si and Al are homogeneously distributed and the ratio Al/Si in the aluminosilicate is the same as in the reaction mixture if the stoichiometric one-to-one ratio for R/Al is used. If SiO_2/R_2O in the Na-silicate solution is equal to or higher than 0.8, the low-temperature reaction yields an amorphous aluminosilicate or ''inorganic polymer glass''. For smaller values of SiO_2/R_2O the Na-aluminosilicates are partially crystalline. Thermomechanical analysis and dynamic mechanical analysis indicate that a variation in the composition of the amorphous aluminosilicates can shift the glass transition over a few hundreds of degrees, with a minimum value of 650 °C.

1. Introduction

The possibility of producing, at ambient temperatures, an amorphous sodium aluminosilicate (called low temperature inorganic polymer glass, LTIPG or IPG) with promising thermomechanical properties was described recently [1, 2]. A few important parameters for establishing the "structure–property" relations of these materials were investigated on a well defined model system [1, 2]. With differential scanning calorimetry (DSC) and magic angle spinning nuclear magnetic resonance (MAS NMR), it was proven that the overall low-temperature reaction between a specific sodium silicate solution (with composition $SiO_2/Na_2O = s = 1.4$; $H_2O/Na_2O = w = 10.0$) and a specific calcined clay, metakaolinite (with composition $(Al_2O_3)(SiO_2)_2(H_2O)_{0.05}$), could be described by the following reaction equation:

$$(Na_2O)(SiO_2)_{1.4}(H_2O)_x + (Al_2O_3)(SiO_2)_2(H_2O)_{0.05}$$

$$\Big\downarrow \text{aq. } (< 100\,^\circ\text{C})$$

$$(Na_2O)(Al_2O_3)(SiO_2)_{3.4}(H_2O)_z$$

x and z being the amount of bound water in the silicate solution and in IPG, respectively (the approximate value of z was 0.4) [1].

The stoichiometry of the reaction was such that the ratio Na/Al or Na_2O/Al_2O_3 in IPG equalled one. Both Al and Si were four-fold coordinated in IPG and

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* Author to whom correspondence should be addressed.

the cross-link density (connectivity) was close to four. The ratio Al/Si in IPG was found to be the same as in the stoichiometric reaction mixture [1].

If all of the Al and Si in the stoichiometric reaction mixture could systematically be incorporated in the aluminosilicate, Al/Si in this solid material would be tuneable via the variable ratio SiO_2/R_2O of the silicate solution. Altering Al/Si in IPG seems interesting for optimizing the material's structure–property relations, since its glass transition temperature (T_g) and thermomechanical properties in general are expected to change significantly with this ratio. Indeed, the thermomechanical properties of other aluminosilicates are largely influenced by their overall composition [3, 4]. The addition of Na, K and Al to silica lowers T_g, but no clear trend is found in the variation of T_g with the ratio Al/Si. Potassium aluminosilicates have a higher T_g than the corresponding sodium aluminosilicates [3, 4].

It can also be expected that H_2O/R_2O and SiO_2/R_2O of the silicate solution influence the low-temperature reaction kinetics, which are of great technological importance for the material's processing (the hardening time, for example, should be variable without changing the final properties too much).

In this paper, DSC will be used to study whether the reaction stoichiometry always obeys R/Al equal to one in the aluminosilicate (for R = Na and K), independently of SiO_2/R_2O of the silicate solution. A comparison of the reactivity of the different silicate solutions will also be made by DSC.

The influence of a varying ratio H_2O/R_2O and SiO_2/R_2O in the silicate solution on the molecular structure of the aluminosilicate will be studied by MAS NMR, Fourier transform infrared spectroscopy (FTIR), cross-polarization (CP) MAS NMR and X-ray diffractometry (XRD).

Thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) will be used to investigate the dependency of the glass transition temperature on the aluminosilicate composition.

2. Experimental details

2.1. Raw materials and processing

The kaolinite used and the production of metakaolinite (Mk) and the silicate solutions (Sil) were described elsewhere [1].

To study the influence of the molar ratio $H_2O/R_2O = w$, it was changed from 6.6 to 18.9 for $R = Na$ and from 8.1 to 21.0 for $R = K$, while the molar ratio $SiO_2/R_2O = s$ was kept constant ($s = 1.4$).

To study the influence of the molar ratio SiO_2/R_2O, values of s ranging from 0.0 to 2.3 for $R = Na$ and from 0.0 to 1.9 for $R = K$ with a constant ratio H_2O/R_2O ($w = 10.0$) were used.

The DSC samples to monitor the low-temperature reaction were always freshly mixed. Aluminosilicate samples for NMR, FTIR, XRD, TMA and DMA were obtained by mixing the silicate solution with Mk in a ratio R_2O/Al_2O_3 of one to one, followed by curing this mixture in a closed mould at room temperature for at least two days [1]. After reaction and before analysis, no washing procedure was applied to the samples to avoid the evacuation of any side products or residual reactants. The aluminosilicate for CP MAS NMR was prepared from a silicate solution with $s = 1.4$ and $w = 10.0$.

2.2. Analytical techniques

2.2.1. Differential scanning calorimetry

The measurements were performed on a Perkin Elmer DSC 7. The purge gas was N_2. Reusable high pressure stainless steel sample pans were used. The scans were performed between -60 and 300 °C with a scan rate of $5\,^{\circ}C\,min^{-1}$.

For the calculation of the reaction enthalpy a straight baseline was used. Each reported reaction enthalpy is the mean value of three independent measurements. The maximum difference for the reaction enthalpy per gram of reaction mixture was 7%.

2.2.2. Nuclear magnetic resonance spectroscopy

^{29}Si and ^{27}Al spectra were obtained on a Bruker AC250 spectrometer operating at 49.70 and 65.18 MHz for the ^{29}Si and ^{27}Al resonance frequencies, respectively. The spectrometer was interfaced with an Aspect-3000 computer and equipped with a MAS broad-band probe for the solid state experiments.

Chemical shifts were referenced to external tetramethylsilane (TMS) in $CDCl_3$ for the ^{29}Si nuclei and to external aqueous $AlCl_3$ for the ^{27}Al nuclei. The chemical shift values were calculated by taking the midpoint of the signal at half height. The accuracy was $+/-$ 0.5 p.p.m.

Rotors of 7 mm diameter and a spinning rate of 5 kHz were used for the solid state experiments. Typically, ^{29}Si MAS NMR spectra were obtained by acquiring 4k data points over a spectral width of 11.1 kHz (acquisition time = 0.2 s), with 1000 scans and a relaxation delay of 2 s. For the ^{27}Al spectra, 4k data points were acquired over a spectral width of 167 kHz (acquisition time = 0.04 s), with 400 scans and a relaxation delay of 0.5 s.

The matching condition for Hartmann–Hahn cross-polarization was set on kaolinite [5].

2.2.3. Fourier transform infrared spectroscopy

The spectra were obtained with a FTIR Perkin Elmer 2000 using KBr pellets (13 mm pellets with 1 mg sample/200 mg KBr). KBr and sample were mixed and ground in a Wig-L-Bug for 3 min and dried overnight at 110 °C before pressing the pellet. For each spectrum, 20 scans with a resolution of $4\,cm^{-1}$ were averaged.

2.2.4. X-ray diffractometry

X-ray diffractograms of powdered samples were recorded on a Philips diffractometer with PW 1820 goniometer, generating a Ni-filtered CuK_α radiation with an applied voltage of 40 kV and a current of 30 mA.

2.2.5. Thermomechanical and dynamic mechanical analysis

Perkin Elmer TMA 7 and DMA 7 were used with a quartz expansion probe (diameter 3 mm). The heating and cooling rate was 5 °C min^{-1}, and the purge gas was He for both TMA and DMA experiments. The applied frequency in all DMA measurements was 1 Hz. Cylindrical samples of LTIPG (with a diameter of 6 mm and an approximate height of 10 mm) were investigated from room temperature up to 1000 °C. For TMA experiments a load of 10 mN was used; for DMA experiments the maximum load (2.5×10^5 Pa static stress and 2.3×10^5 Pa dynamic stress) was used.

3. Results and discussion

3.1. The low-temperature reaction and its stoichiometry

In a previous paper, it was shown that the stoichiometric ratio Sil/Mk equalled one in the case of the low-temperature reaction of Mk with a specific sodium silicate solution with $s = 1.4$ and $w = 10.0$ [1]. In this work, the influence of the silicate solution's composition, using the same Mk, on the proposed reaction stoichiometry is verified with DSC.

To investigate the influence of the molar ratio $H_2O/R_2O = w$ of the silicate solution on the reaction enthalpy, the enthalpies measured with DSC are expressed per gram Mk (see Table I). It will be shown in the next section that the reaction product is independent of the water content and therefore the reaction enthalpy is not likely to change with the water content. For the K-silicates the reaction enthalpies are indeed almost constant over the range measured (see Table I; $|\Delta H|$ *c.* 500 J g^{-1} Mk). For the Na-silicates, the absolute values of the reaction enthalpies are not constant and apparently go through a maximum. The observed minimum values ($|\Delta H|$ *c.* 260 J g^{-1} Mk) are smaller and the maximum values ($|\Delta H|$ *c.* 580 J g^{-1} Mk) comparable to the values measured for the K-silicates.

TABLE I Reaction enthalpy per gram Mk as a function of the molar ratio $H_2O/R_2O = w$ ($s = 1.4$)

w (H_2O/R_2O) (mole/mole)	$-\Delta H$ (R = Na) (J g^{-1} Mk)	$-\Delta H$ (R = K) (J g^{-1} Mk)
6.6	260	
8.1	440	470
8.8	490	
9.5	500	480
10.0	580	
11.2	550	
12.1		560
12.2	570	
14.2		540
15.1	390	
16.9		460
18.9	270	
21.0		440

For high water contents, the DSC thermogram shows a double peak for the polymerization exotherm at about 100 °C (see Fig. 1). The largest part of the reaction exotherm is shifted above 100 °C, indicating a smaller reactivity for high water contents. This was also noticed during sample preparation for MAS NMR: silicates with water contents higher than $w = 18.9$ (for R = Na) and $w = 21.0$ (for R = K) could not be prepared because (i) the reactivity of the silicate becomes so small that the mixture does not react within a reasonable time scale, even at 60 °C; and (ii) sedimentation of Mk during the reaction leads to inhomogeneous samples.

Smaller water contents than $w = 6.6$ (for R = Na) and $w = 8.1$ (for R = K) could not be investigated because the mixing of silicate with Mk becomes impossible. A bad wetting of the Mk grains could also lead to incomplete reaction, explaining the small $|\Delta H|$ of 260 J g^{-1} Mk for the Na-Sil with the lowest water content ($w = 6.6$). Therefore, it is concluded that the observed change in reaction enthalpy as a function of the water content is due to an incomplete reaction of Mk with the silicate. This effect is most pronounced in the case of the Na-silicates, probably because the higher viscosity of Na-Sil compared to K-Sil makes mixing extremely difficult at low water contents.

The upper limit for the molar ratio $SiO_2/R_2O = s$ of the investigated silicate solutions is also determined by the reaction rate, since the hardening process becomes slower with increasing s. For values of s above 2.3 for Na-Sil and 1.9 for K-Sil the reaction obviously does not go to completion in a time scale of days at room temperature. The influence of s is illustrated in the DSC thermograms of Fig. 2. The exotherm of the polymerization shifts to higher temperatures and

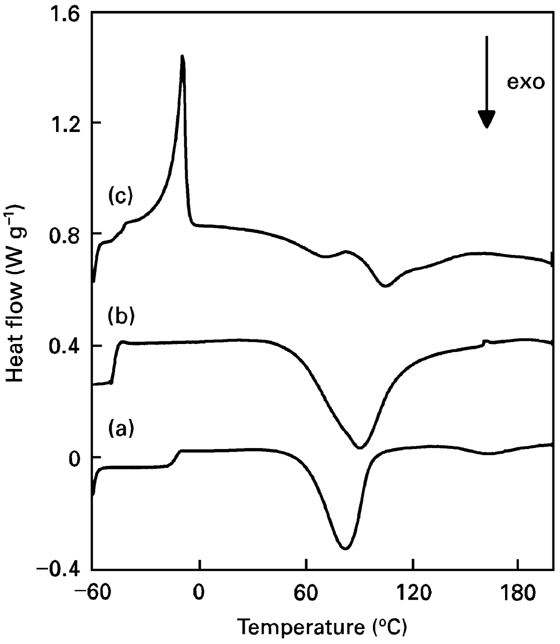

Figure 1 Comparison of DSC thermograms for the reaction of Mk with Na-silicate solutions with variable w ($s = 1.4$): (a) 6.6, (b) 9.7 and (c) 12.2.

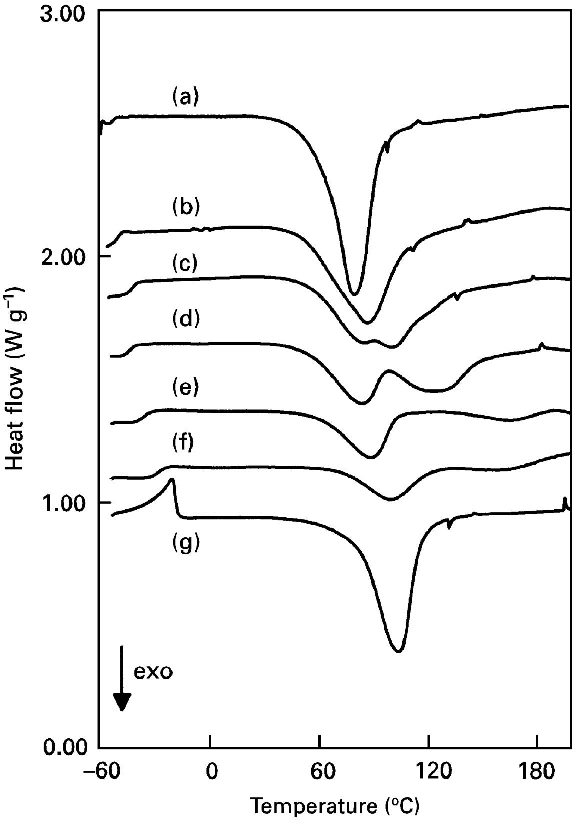

Figure 2 Comparison of DSC thermograms for the reaction of Mk with Na-silicate solutions with variable s ($w = 10.0$): (a) 1.0, (b) 1.4, (c) 1.6, (d) 1.7, (e) 1.9, (f) 2.3 and (g) K-Sil with $s = 1.4$.

TABLE II Reaction enthalpy for the low-temperature reaction of Mk with Na-Sil with $s = 1.0$ and $w = 10.0$, Na-Sil with $s = 0.0$ and $w = 10.0$, and K-Sil with $s = 1.7$ and $w = 11.2$ as a function of the molar ratio Sil/Mk

Sil/Mk (mole/mole)	$-\Delta H$ (J g^{-1} mixture) (R = Na; $s = 1.0$; $w = 10.0$)	$-\Delta H$ (J g^{-1} mixture) (R = Na; $s = 0.0$; $w = 10.0$)	$-\Delta H$ (J g^{-1} mixture) (R = K; $s = 1.7$; $w = 11.2$)
0.57			156
0.70	210		
0.71			167
0.73		262	
0.80	247		
0.86			182
0.92		326	
1.00	258	347	190
1.14			179
1.29			171
1.43			152
1.50	214	302	
1.70			129
2.00		255	
2.20	157		
2.26			113
2.82			92
3.00	151	178	

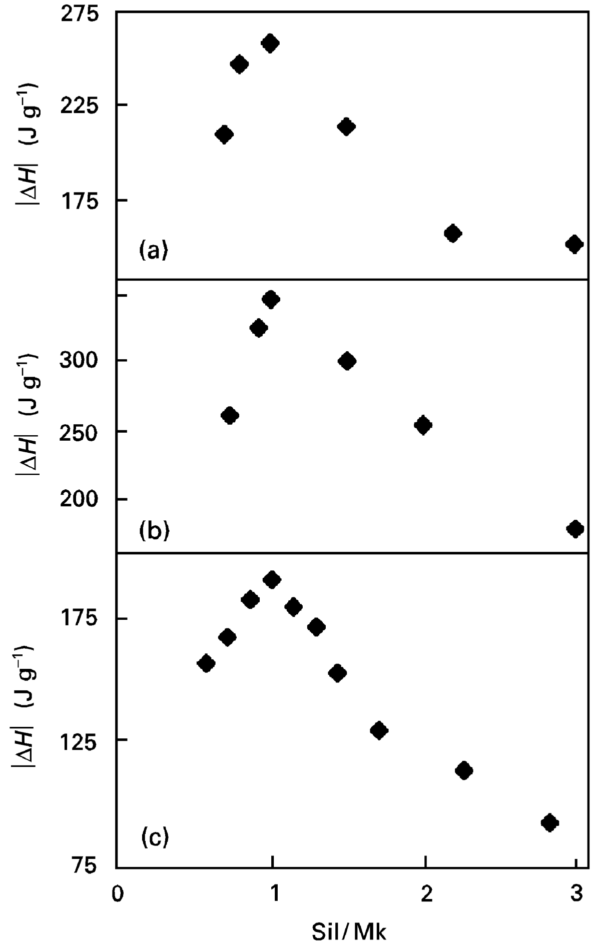

Figure 3 Reaction enthalpy as a function of the Sil/Mk ratio for: (a) Na-Sil/Mk with $s = 1.0$ and $w = 10.0$, (b) Na-Sil/Mk with $s = 0.0$ and $w = 10.0$, and (c) K-Sil/Mk with $s = 1.7$ and $w = 11.2$.

splits up with increasing s. The reaction of Mk with K-Sil is also slower than with Na-Sil for the same s and w values of the silicate (compare Fig. 2b and g).

Figs 1 and 2 also show the influence of the composition on the initial glass transition temperature (T_g) of Sil. As can be seen from Fig. 1, T_g decreases for increasing water content, and for high water contents, e.g. $w = 12.2$, Sil crystallizes during cooling from room temperature and a melting peak emerges in the subsequent heating (Fig. 1c). For K-Sil (see Fig. 2g) a melting endotherm is already observed at lower water content ($w = 10.0$): T_g for this K-Sil is *c.* −90 °C and its viscosity at room temperature is much lower than that of the comparable Na-Sil of Fig. 2b. Fig. 2 shows that T_g of Na-Sil increases with increasing s. The viscosity at room temperature of these solutions also increases with s. Consequently the mixing of K-Sil with Mk, compared to Na-Sil, is much easier.

To study the influence of the silicate composition on the reaction stoichiometry with DSC, the reaction enthalpy of the low-temperature cure of Mk with two sodium silicate solutions ($w = 10.0$ and $s = 1.0$ and 0.0, respectively; note that the latter is not a silicate but a pure NaOH solution) and a potassium silicate solution ($s = 1.7$ and $w = 11.2$) is measured as a function of the ratio Sil/Mk. All measured reaction enthalpies (see Table II and Fig. 3) go through a maximum for a ratio Sil/Mk of one. This observation proves that for each silicate solution the optimum ratio Sil/Mk is fixed by the ratio R/Al or R_2O/Al_2O_3 in the aluminosilicate, that has to be one for R = Na or K, and not by the reaction mixture's overall ratio Al/Si which varies according to the silicate composition (for more details on this DSC method, see also [1]). These DSC results however do not indicate whether, with stoichiometric conditions, all Si (from Sil and Mk) and all Al (from Mk) of the initial reaction mixture is incorporated in the aluminosilicate structure, or whether some residual Si and/or Al remain in solution. This question is handled in the next section.

3.2. Short range order in the aluminosilicates

The chemical short-range order, defined as the kind and number of nearest neighbours [6], is studied by MAS NMR and FTIR for all synthesized aluminosilicates, giving information on their molecular structure and their global ratio Al/Si. For this purpose, the aluminosilicates were synthesized with silicates of varying *w* or *s* values, but always according to stoichiometric reaction conditions.

As can be seen from Table III (for Na-aluminosilicates) and Table IV (for K-aluminosilicates), neither the chemical shift nor the "full width at half maximum" (FWHM) of the ^{27}Al and ^{29}Si NMR signals are significantly influenced by changing *w* of the silicate solutions with constant $s (s = 1.4)$. The peak broadening of the ^{29}Si NMR signals of the Na-aluminosilicates for values of *w* smaller than 8.1 (see Table III) points in the same direction as the DSC results of Section 3.1.

The observed invariance for the ^{29}Si NMR signal (the maximum difference between two samples in the same series is 0.5 p.p.m.) indicates that the amount of SiOH groups in the aluminosilicates is independent of *w* of the silicate solution. Indeed, if the amount of bound water in the form of SiOH groups could change with *w* of the silicate solution, the chemical shift would also change because one additional SiOH group per Q-unit would increase the chemical shift by *c*. 10 p.p.m. [7].

It should be noted that the ^{29}Si NMR chemical shifts are about 1 p.p.m. lower for K-aluminosilicates than for Na-aluminosilicates, an observation in agreement with the literature [7], while the opposite seems valid (although less pronounced) for the ^{27}Al NMR chemical shifts.

^{27}Al and ^{29}Si MAS NMR data for aluminosilicates prepared from Mk and silicate solutions with different $s (w = 10.0)$ are summarized in Tables V and VI. Note that the mixing ratio Sil/Mk is always stoichiometric; if not, residual reactants should be detected as additives in the synthesized aluminosilicates [1]. Typical spectra are shown in Figs 4 and 5. It is important that all spectra contain only one broad peak due to the amorphous character of the material, and that no fine-structure is revealed in the signals, except for *s* close to 0.0.

The ^{27}Al chemical shift of all aluminosilicates, between 53 and 63 p.p.m. is always in the range of four-fold coordinated Al surrounded by four Si atoms [7]. The fact that Al is four-fold coordinated is in accord with the observation that the ratio R/Al equals one for R = Na or K: as already pointed out [1], each AlO_4 unit introduces one negative charge that is compensated by the cation R.

For both Na- and K-aluminosilicates, the ^{29}Si resonance position shifts to higher field with increasing *s* value (see Tables V and VI and Fig. 5). The average amount of Al bound to Si (defined as *m* or Al, Si ordering), assuming that all Si and Al of the reaction

TABLE III MAS NMR results for Na-aluminosilicates: influence of the molar ratio $H_2O/Na_2O = w$ on the ^{27}Al and ^{29}Si signals. The peak width is the "full width at half maximum" (FWHM)

w (H_2O/R_2O) (mole/mole)	Si chemical shift (p.p.m.)	Si peak width (p.p.m.)	Al chemical shift (p.p.m.)	Al peak width (p.p.m.)
6.6	− 91	20	56	16
8.1	− 91	18	56	16
8.8	− 91	16	55	16
9.5	− 90.5	16	56	16
11.2	− 91	16	56	16
12.2	− 91	16	55	17
15.1	− 91	16	55	17
18.9	− 91	16	55	16

TABLE IV MAS NMR results for K-aluminosilicates: influence of the molar ratio $H_2O/K_2O = w$ on the ^{27}Al and ^{29}Si signals. The peak width is the "full width at half maximum" (FWHM)

w (H_2O/R_2O) (mole/mole)	Si chemical shift (p.p.m.)	Si peak width (p.p.m.)	Al chemical shift (p.p.m.)	Al peak width (p.p.m.)
8.1	− 92	16	56	16
9.5	− 91.5	16	56	16
12.1	− 91.5	16	56	16
14.3	− 92	16	57	16
16.9	− 91.5	16	56	16
21.0	− 92	16	56	16

TABLE V MAS NMR and FTIR results for Na-aluminosilicates: influence of the molar ratio $SiO_2/Na_2O = s$ on the ^{27}Al and ^{29}Si signals and on the IR absorptions. The value m is calculated according to Equation 1. The peak width is the "full width at half maximum" (FWHM)

s SiO_2/Na_2O (mole/mole)	Al chemical shift (p.p.m.)	Al peak width (p.p.m.)	Si chemical shift (p.p.m.)	Si peak width (p.p.m.)	m (−)	Si–O stretching (cm^{-1})	Si–O bending (cm^{-1})
0.0	63	7	− 85	4	4.00	993	436
0.2	58	13	− 86	4	3.64	995	436
0.4	58	13	− 87	6	3.33	1003	455
0.8	57	17	− 88	13	2.86		
1.0	57	17	− 88	16	2.67	1007	448
1.2	55	17	− 90	16	2.50	1009	444
1.4	56	17	− 91	16	2.35	1014	444
1.5	57	17	− 91.5	17	2.29	1013	450
1.7	55	19	− 92	16	2.16	1010	450
1.9	55	17	− 92.5	17	2.05	1019	446
2.1	55	18	− 94	16	1.95	1023	452
2.3	53	20	− 95	17	1.86	1034	450

TABLE VI MAS NMR and FTIR results for K-aluminosilicates: influence of the molar ratio $SiO_2/K_2O = s$ on the ^{27}Al and ^{29}Si signals and on the IR absorptions. The value m is calculated according to Equation 1. The peak width is the "full width at half maximum" (FWHM)

s SiO_2/K_2O (mole/mole)	Al chemical shift (p.p.m.)	Al peak width (p.p.m.)	Si chemical shift (p.p.m.)	Si peak width (p.p.m.)	m (−)	Si–O stretching (cm^{-1})	Si–O bending (cm^{-1})
0.0	57	16	− 86	8	4.00	1051	459
0.2	58	16	− 86	10	3.64	1011	447
0.4	57	16	− 87	11	3.33	1003	447
0.6	57	16	− 87	12	3.08		
0.8	57	14	− 89	13	2.86	1011	444
1.0	56	16	− 89.5	14	2.67	1014	447
1.2	56	16	− 91	15	2.50	1019	447
1.4	57	16	− 92	16	2.35	1019	443
1.5	56	14	− 92.5	16	2.29		
1.6	55	16	− 93	16	2.22		
1.7	56	15	− 93	16	2.16	1018	446
1.9	56	15	− 93.5	16	2.05	1025	446

mixture is built in and all Al is tetrahedrally surrounded by 4 Si atoms, is calculated by Equation 1:

$$m = \frac{2n'}{2 + k_{st}s} \tag{1}$$

where n' is the cross-link density (connectivity) of Al in the aluminosilicate ($n' = 4$), s is the ratio SiO_2/R_2O in Sil and k_{st} is the stoichiometric ratio Sil/Mk ($k_{st} = 1$) [1].

With increasing s, the value of m or the average Al substitution around Si decreases (see Tables V and VI). The calculated values of m are plotted in Fig. 6 against the chemical shift of the ^{29}Si NMR signal. A steady decrease in chemical shift is observed for decreasing degree of Al substitution. The dependency of the Si resonance position on the number of surrounding Al atoms is well known [7]. The indicated literature values [8, 9] in Fig. 6 are in line with the attributions of this work. The values of m, being calculated from the global ratio Al/Si in the stoichiometric reaction mixture, suggests that Al/Si in the aluminosilicate is the same as in the stoichiometric reaction mixture for all Na- and K-silicate compositions studied. This statement, that in stoichiometric reaction conditions all Si and Al of the reaction mixture are incorporated in the resulting aluminosilicate, is in agreement with the observation of a unique peak without fine-structure in all the NMR signals. It means that neither Al nor Si is detected in side products of different chemical composition [1].

These NMR findings are supported by IR measurements on the aluminosilicates. An increase of the Si–O stretching absorption frequency (at about 1000 cm^{-1}) with increasing s is observed (see Table V) for Na-aluminosilicates. The same trend is observed for K-aluminosilicates from s values of 0.4 on (see Table VI). The much higher frequency for $s = 0$ will be discussed later in Section 3.3. This IR absorption is a coupled asymmetric Si(Al)–O stretching vibration. The fact that the asymmetric Si–O stretch of glassy silica (1100 cm^{-1}) shifts to lower frequencies, when substitution of Si by Al takes place, is described in the literature [10–12]. This shift, however, gets less pronounced with increasing Al content, especially above an Al content of 20 at % [12] (which is the case for all samples in this work). Therefore, the increase of the IR absorption wavenumber with increasing s can again

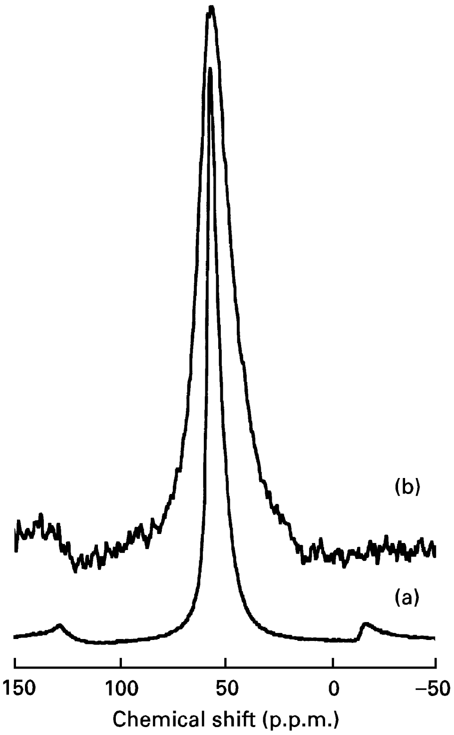

Figure 4 ^{27}Al MAS NMR spectra of Na-aluminosilicates with: (a) $s = 0.0$ and (b) $s = 2.3$.

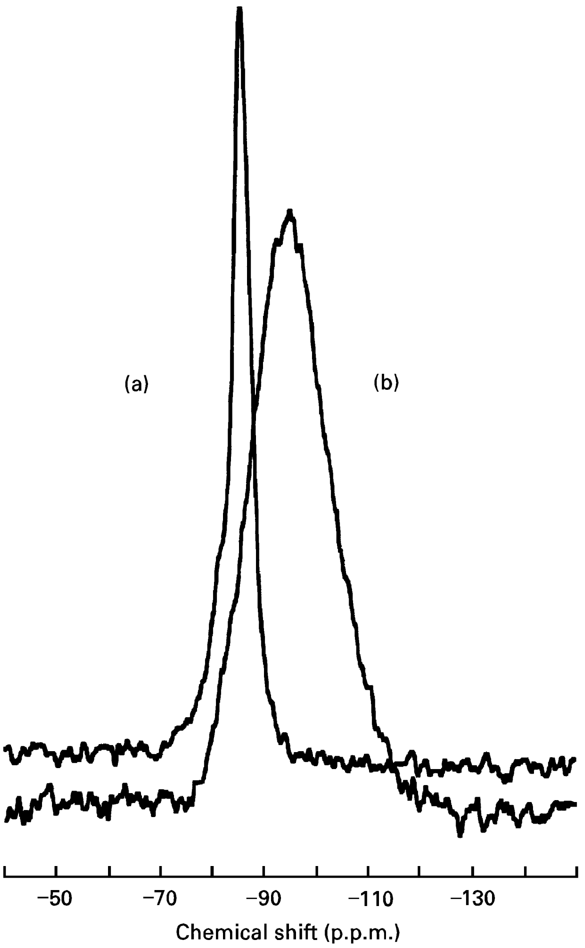

Figure 5 ^{29}Si MAS NMR spectra of Na-aluminosilicates with: (a) $s = 0.0$ and (b) $s = 2.3$.

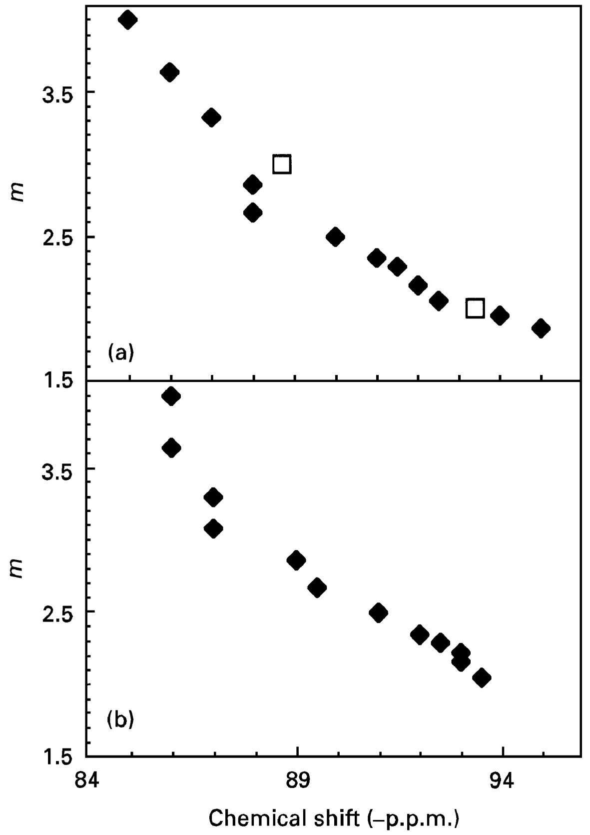

Figure 6 Amount of Al surrounding SiO_4 (m) as a function of the ^{29}Si chemical shift for: (a) Na-aluminosilicates and (b) K-aluminosilicates: ◆ this work; □ literature values [8, 9].

be explained as a decreasing Al substitution (or decreasing m) in the aluminosilicate network. So, NMR and FTIR measurements are in agreement and the continuous evolution of NMR and FTIR signals as a function of s suggests that Si and Al are always uniformly distributed and that no segregation of Al rich or poor environments is likely [12].

It can be concluded that in stoichiometric conditions the ratio Al/Si in the synthesized aluminosilicates decreases with s of the silicate solution and therefore is tuneable. The overall low-temperature reaction equation between a silicate solution and metakaolinite, proposed for the model system [1], can now be generalized:

$$(R_2O)(SiO_2)_s(H_2O)_x + (Al_2O_3)(SiO_2)_2(H_2O)_{0.05}$$

$$\Big\downarrow \text{aq. } (< 100\,^{\circ}\text{C})$$

$$(R_2O)(Al_2O_3)(SiO_2)_y(H_2O)_z \qquad (2)$$

where $y = SiO_{2,\text{total}}/Al_2O_3 = (2 + s)$ and z is the amount of bound water in the aluminosilicate (the approximate value of z is 0.4 if $s = 1.4$ [1]).

The presence of ‘bound’ water, especially in the form of SiOH groups, makes cross-polarization (^{1}H–^{29}Si) MAS NMR possible. The ^{29}Si CP MAS NMR signal (Fig. 7a) originates from Si-nuclei that are close enough to H-nuclei for cross-polarization to occur. To a first approximation, it can be assumed that only SiOH groups contribute to the ^{29}Si CP MAS NMR signal. This ^{29}Si CP MAS NMR signal is

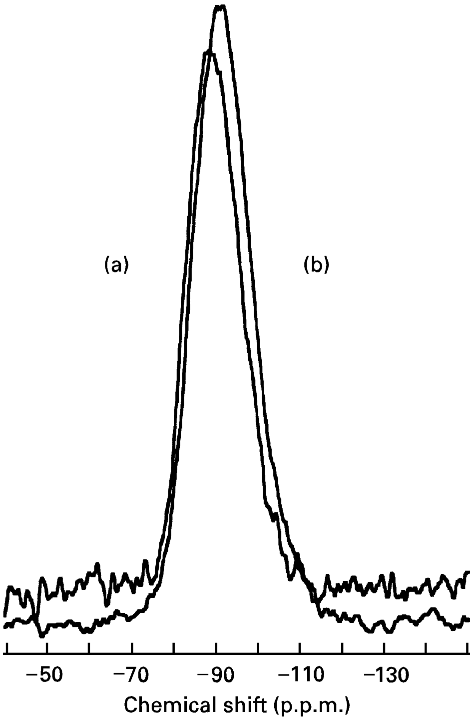

Figure 7 Amount of SiOH groups in the aluminosilicate ($s = 1.4$): (a) ^{29}Si CP MAS NMR spectrum and (b) ^{29}Si MAS NMR spectrum.

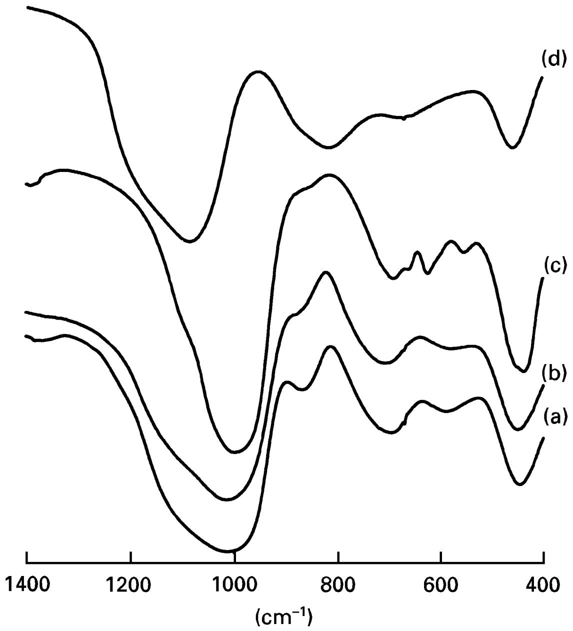

Figure 8 FTIR spectra of different aluminosilicates: (a) K-aluminosilicates ($s = 1.4$), (b) Na-aluminosilicates ($s = 1.4$), (c) Na-aluminosilicates ($s = 0.0$) and (d) Mk.

completely overlapping with the ^{29}Si MAS NMR signal (Fig. 7b). Since no separate resonance is observed, a reliable quantification of the number of SiOH groups seems impossible or at least very difficult. Anyhow, the small signal-to-noise level for the ^{29}Si CP MAS NMR spectrum, proportional to the quantity of SiOH groups, indicates that only a small number of SiOH groups are present. Therefore the value of z in Equation 2 should be small compared to the initial amount of water in the reaction mixture and only a few non-bridging oxygen atoms should be present in the synthesized aluminosilicate. So, the CP MAS NMR experiment at least does not contradict the value $z = 0.4$ proposed for the model system from thermogravimetric analysis [1].

3.3. Additional structural analysis of the aluminosilicates

The small changes in the shift of the ^{27}Al MAS NMR signal as a function of s, especially for the Na-aluminosilicates (compare Tables V and VI), can be due to second nearest neighbour effects: in the case of $s = 0.0$, Mk is the only source of Si and Al and both elements are present in equal amounts. As already demonstrated m equals four in this case, so each SiO_4 tetrahedron is surrounded by four Al atoms and thus the second nearest neighbours of each AlO_4 unit are always AlO_4 units. With increasing s, these AlO_4 units are gradually replaced by SiO_4 units. So, the chemical environment of the Al nuclei is altered but also the regularity of the structure is lowered by increasing s: bond angles and bond distances change because of Al substitution by Si [13], which could be a reason for the change in the ^{27}Al MAS NMR signal position and its peak width. For Na-aluminosilicates FWHM of the ^{27}Al MAS NMR signal increases from 7 p.p.m. for $s = 0.0$ to 17 p.p.m. and more for $s \geqslant 0.8$, but for the K-aluminosilicates it is rather constant (about 16 p.p.m.).

FWHM of the ^{29}Si MAS NMR signal increases with decreasing m from 4 p.p.m. (Na-aluminosilicates) or 8 p.p.m. (K-aluminosilicates) to a value of 16 p.p.m. for m values of 2.5 and lower. This broadening can again be explained by a decreasing regularity of the molecular structure, or more explicitly here by the number of different Q-units that can contribute to the signal. For a m value of four, only Q^4(4Al) can contribute to the spectrum. The differentiation in Q-units can indeed be larger for the compositions with m between 1 and 3. The total signal is thus the sum of several discrete overlapping peaks and therefore broader.

K-aluminosilicates and Na-aluminosilicates, prepared from silicate solutions with s higher or equal to 0.8, show similar FTIR spectra (see Fig. 8a and b). The broadness of the absorption peaks reveals the amorphous character of the material. The typical Al^{IV} absorption in the metakaolinite spectrum at 810 cm^{-1} (see Fig. 8d) completely disappears and at this frequency the transmission is the highest. Compared to Mk, the shift to lower frequencies of the coupled asymmetric Si(Al)–O stretching vibration (at about 1000 cm^{-1}) is due to the increasing Al content [10–12] ($m = 1$ for Mk [14–16], and m is always higher for the aluminosilicates of this work, see Tables V and VI).

The absorption band at 700 cm^{-1} is also a coupled Si, Al vibration [12, 17] and according to Gervais *et al.* [12] the most sensitive to Al substitution, but not above 20 at %. Since our samples contain 25–33 at % Al, this is probably the reason that no shift of this band with s is seen.

The Si–O–Si bending peak at *c*. 450 cm^{-1} does not shift with the Al content (see Tables V and VI), which is also consistent with the literature [10]. At present, the peak at 580 cm^{-1}, also independent of s, cannot be assigned.

No sharp peaks in the hydroxyl stretching region are seen (not shown in Fig. 8). The broad absorption, again typical for amorphous materials, around 3400 cm^{-1} is ascribed to both bound and free water [18], and is thus not suitable for quantifying the amount of bound water. The absence of any large absorption in the region 950–800 cm^{-1} (only a small shoulder is detected for Na-aluminosilicates and a small peak for K-aluminosilicates) indicates that there are no, or only a few, non-bridging oxygen atoms [10, 12] and confirms the ^{29}Si CP MAS NMR result of Section 3.2.

In the FTIR spectra of aluminosilicates, prepared from silicate solutions with s smaller than 0.8, additional absorptions and peak sharpening are seen (see Fig. 8c). Sharper peaks are an indication of a more regular structure [19]. The NMR results previously discussed point in the same direction (compare Fig. 4a and b and Fig. 5a and b).

In the X-ray diffractograms of Na-aluminosilicates, prepared from silicate solutions with s smaller than 0.8, sharp peaks of crystals are detected (see Fig. 9). These aluminosilicates are thus not totally amorphous. Comparing the height of the discrete crystalline diffraction peaks with the underlying amorphous part, it can be concluded qualitatively that the crystalline fraction increases with decreasing s.

These results confirm the findings of NMR and FTIR, where peak sharpening was related to a more regular structure. Indeed, for $s = 0.0$, the ratio Al/Si is unity, and because each AlO_4 unit is surrounded by four Si atoms, a network of alternating SiO_4 and AlO_4 units is formed. It is plausible that this regular network contains crystalline domains. Note that the reaction of kaolinite (crystalline) with NaOH yields hydroxysodalite (crystalline) [20]. When a "silicate" solution with $s = 0.0$ (pure NaOH) is reacted with Mk (amorphous), traces of hydroxysodalite are detected with FTIR and XRD in the synthesized partially crystalline aluminosilicate. For the analogous K-aluminosilicate, traces of crystalline products are also found, but the type of crystals have not yet been identified. The higher frequency of the IR asymmetric Si–O stretching absorption for the K-aluminosilicate with $s = 0$ (see Table VI) probably originates from these crystals.

For Na-aluminosilicates, the formation of crystals during polymerization is more complicated than for K-aluminosilicates. For Na-silicates with s between 0.2 and 0.8, liquid–crystal phase separation is likely to occur [21], especially when the undercooled liquids are mixed with Mk. In a DSC scan, melting of Na-silicate crystals in the reaction mixture with Mk is seen as an endothermic signal at the beginning of the polymerization exotherm (see Fig. 10).

To make sure that the crystals, detected for some of the aluminosilicates in Fig. 9, did not originate from their respective Na-silicates (with s smaller than 0.8), aluminosilicate samples were prepared and thermally treated in DSC (heated up to 180 °C, far above the melting point of these Na-silicate crystals) before further investigation with XRD. The same diffraction lines were observed.

An important conclusion of these XRD, NMR and FTIR results is that the aluminosilicates prepared from silicate solutions with s less than 0.8 are not fully amorphous and that the term "inorganic polymer glass" used for the model compound [1, 2] is thus not applicable to these aluminosilicates. Because of their inferior mechanical properties, these less than fully amorphous (or partially crystalline) aluminosilicates are not further investigated at present.

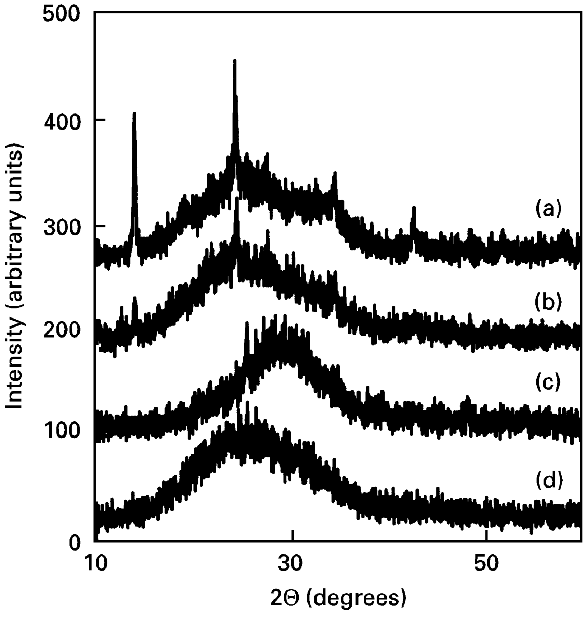

Figure 9 X-ray diffractograms of aluminosilicates prepared from Na-silicates with: (a) $s = 0.0$, (b) $s = 0.4$, (c) $s = 0.8$ and (d) $s = 1.4$. The diffraction lines for $s = 0.8$ originate from the TiO_2 impurity in Mk.

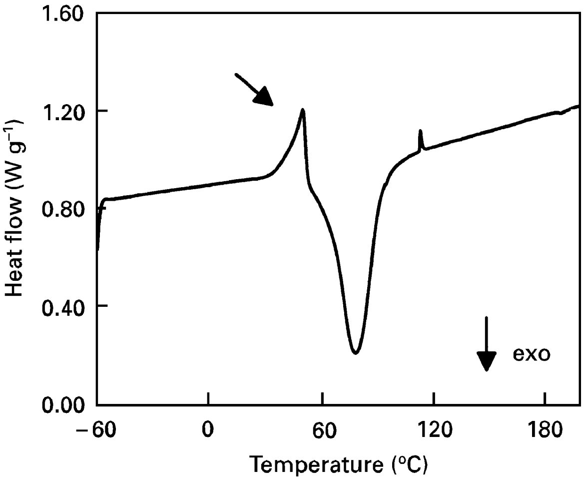

Figure 10 DSC thermogram of the low-temperature polymerization of Mk with Na-Sil with $s = 0.8$ and $w = 10.0$. Na-Sil crystals, formed during sample preparation, melt at the onset of polymerization between 30 and 50 °C (see arrow).

3.4. High-temperature properties of the aluminosilicates

The dependency of the thermomechanical behaviour, especially T_g, on the composition of IPG is demonstrated in Fig. 11.

TMA and DMA thermograms are given for IPG produced from Na-Sil with $s = 1.4$ ("model compound") and $s = 1.9$, and from K-Sil with $s = 1.4$. During the first heating after production, all IPG compositions studied by TMA show a large shrinkage due to the evaporation of water as discussed in a previous paper [2]. The onset of the second shrinkage during the first heating, compared to the model compound (see Fig. 11a; onset at *c.* 650 °C), is at a higher temperature for Na-IPG prepared from Na-Sil with $s = 1.9$ (see Fig. 11b; onset at *c.* 800 °C), and at an even higher temperature for K-IPG (see Fig. 11c; onset at *c.* 900 °C). This second onset of shrinkage is in the neighbourhood of T_g. The exact position of T_g is difficult to localize in a second heating because (i) the increase in expansion coefficient in the transition region around T_g is small (only a factor of 2 [2]), and (ii) T_g for the latter two compositions is close to the experimental limit of the TMA measuring device. The peak of the loss modulus measured by DMA for these two compositions is above the measuring limit of the DMA equipment too (see Fig. 11b and c). However, these results confirm that T_g is higher for K-IPG than for Na-IPG, and also for IPG compositions with a decreased Al/Si ratio [3, 4]. It is important that this "structure–high-temperature property" relation for the inorganic polymer glasses studied can be tuned by the low-temperature production of these materials.

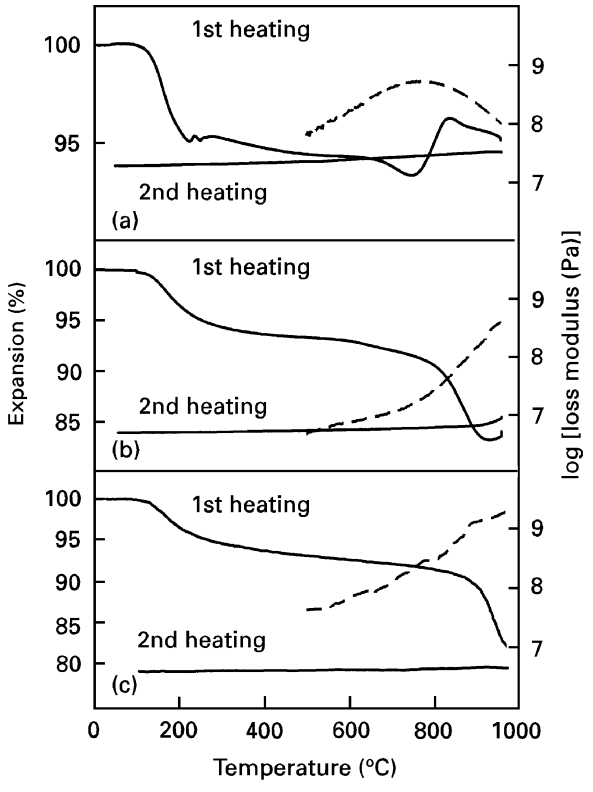

Figure 11 TMA (expansion) (——) and DMA (loss modulus) (– – –) thermograms of IPG prepared from: (a) Na-Sil with $s = 1.4$ (model compound), (b) Na-Sil with $s = 1.9$ and (c) K-Sil with $s = 1.4$.

4. Conclusions

DSC results prove that the stoichiometry of the reaction of Mk with a sodium or potassium silicate solution with a varying ratio SiO_2/R_2O is such that one cation (Na or K) from the silicate solution is needed for each Al from Mk.

If the ratio H_2O/R_2O of the silicate solution is varied, the reaction enthalpy of the reaction expressed per gram Mk is rather constant for K-Sil, as expected, but goes through an apparent maximum for Na-Sil. The most plausible reason for this evolution is the fact that the reaction conversion is not reaching 100% for silicate solutions with too low or too high water contents. In the former case, this is explained by insufficient mixing because of the high viscosity of the Na-silicate solution. In the latter case, sedimentation of Mk renders inhomogeneous samples.

According to ^{27}Al MAS NMR and ^{29}Si MAS NMR the ratio H_2O/R_2O of the silicate solution has no influence on the molecular structure of the aluminosilicate formed.

^{27}Al MAS NMR shows that Al is tetrahedrally coordinated over the whole range of aluminosilicates studied. The most important conclusion of this study is that the ratio Al/Si of the aluminosilicates is the same as in the reaction mixture if the stoichiometric ratio of R/Al equal to one is used. The ratio Al/Si of the synthesized aluminosilicates is thus tuneable via the ratio SiO_2/R_2O of the silicate solution. This conclusion and the fact that Si and Al are uniformly distributed are supported by FTIR measurements.

At present, the amount of SiOH groups could not be determined quantitatively by ^{29}Si CP MAS NMR or by FTIR, but it should be small.

XRD, NMR and FTIR results indicate that the Na-aluminosilicates prepared from silicate solutions with SiO_2/R_2O less than 0.8 are not totally amorphous and should not be considered as "inorganic polymer glasses" for construction or highly demanding thermomechanical applications.

TMA and DMA experiments show that T_g of IPG depends on its aluminosilicate composition, and that T_g can be shifted over some hundreds of degrees by the low-temperature production route using silicate solutions of the appropriate composition.

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