NMR and FTIR Characterization of Sol-Gel Derived Ternary Oxide Glasses in the System $BaO-TiO_2-SiO_2$

M. Feike* and K. Meise-Gresch

Institut für Physikalische Chemie der Westfälischen Wilhelms-Universität, Schlossplatz 4/7,
D-48149 Münster, Germany

Qi Chen** and G.H. Frischat

Institut für Nichtmetallische Werkstoffe, Technische Universität Clausthal, Zehntnerstrasse 2A,
D-38678 Clausthal-Zellerfeld, Germany

Z. Naturforsch. **50a,** 837–844 (1995); received January 5, 1995

Dedicated to Professor Werner Müller-Warmuth on the occasion of his 65th birthday

The annealing history of glasses in the system (20–40) $BaO-40TiO_2(40-20)SiO_2$ has been monitored by ^{29}Si MAS NMR and FTIR spectroscopy from the dried gel to the final glassy state. Assignment of chemical shifts to specific building units has been facilitated by comparative studies of the limiting less complex binary silicate systems. From the NMR spectra at various compositions appreciable condensation to a three-dimensional network is inferred already at low drying temperatures. Processes like the pyrolysis of acetate rests of the starting materials and modification of the silicate structure due to Ba^{2+} cations have been mirrored in the spectra of both methods for samples annealed at intermediate temperatures. The microstructure of the final gel glass of the ternary system has been determined spectroscopically to consist of silicate and titanate species typical of crystalline fresnoite, whereas remaining amounts of TiO_2 and SiO_2 develop a separate network each. Only small amounts of Si–O–Ti linkages have been recognized in the vibrational absorptions; they vanish at higher annealing stages.

1. Introduction

Conventional glasses of the composition $BaO-TiO_2-SiO_2$ are known to exhibit among other properties of technological importance, such as high refractive indices and high deformation temperatures, an exceptionally good chemical durability [1]. New alkali resistant glassy coatings of the mixed oxides $BaO-TiO_2-SiO_2$ via the sol-gel process have recently been developed [2]. These coatings may be applied, for example, to glass fibres used to reinforce portland cement as a protection against attack in highly alkaline solutions arising from the cement surroundings.

The sol-gel dip process allows the formation of multicomponent coatings with compositions not accessible by melting. Furthermore, a high chemical homogeneity as well as a tailored microstructure of the deposited films can be achieved by this alternative procedure [3].

Application of high resolution solid state NMR spectroscopy to elucidate the structure of glasses is well known [4–5]. In this laboratory NMR investigations on gel-derived glasses have been performed previously [6–8], one of them dealing with the alkali resistant ternary oxide composition $SiO_2-TiO_2-ZrO_2$ [6]. An attempt is made to clarify the structural conversion in the sol-gel-process of the present system, mainly by the well-established ^{29}Si magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy [5]. As an important complementary method, FTIR measurements have been carried out additionally. A combined spectroscopical effort is made to find out how the oxygen coordination polyhedra of the network formers are interlinked and in which way the network modifying Ba^{2+} cations will interfere in this process.

Coatings composed of (20–40) $BaO-40TiO_2-(40-20)SiO_2$ given in mol% [2] are known to exhibit the best resistance against alkaline corrosion. For sensitivity reason bulk material instead of thin films was synthesized for the NMR investigations, using identical preparation conditions as outlined in [2]. They had been optimized for the dip coating procedure. In addi-

---

* Present address: Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany.
** Permanent address: East China University of Science and Technology, Shanghai, China.

Reprint requests to Dr. K. Meise-Gresch.

0932-0784 / 95 / 0900-0837 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

tion the binary systems $BaO-SiO_2$ and TiO_2-SiO_2 have been prepared via the same route and studied for a better understanding of the more complex ternary oxide glass-system.

2. Experimental

2.1 *Sample Preparation*

All chemicals have been purchased from the Merck Company. According to the compositions listed in Table 1 several solutions were prepared as follows. At ambient temperature a liquid mixture of tetraethylorthosilicate (TEOS), anhydrous ethanol (EtOH), glacial acetic acid (HAc) and water with a molar ratio of H_2O:TEOS = 2:1 was vigorously agitated for 120 min. After this step, $Ti(OC_4H_9)_4$ mixed with ethanol was added into the TEOS-solution while stirring for another 30 min. Barium acetate dissolved in acetic acid and water was added under continuous stirring. The clear solution was diluted by ethanol to a concentration of 0.4–0.6 mol/l. A molar ratio of the total water content to metal alkoxides and acetate of 4 is maintained. The pH of the prepared solutions ranged from 4 to 5.5. After final stirring (60 min) the solutions were aged in a covered plastic container at room temperature for 1 day, then dried at 60 °C for 4 days. For further annealing the dried gels were heated at a rate of 1 K/min to the desired temperature and kept there for 10 h. To achieve a homogeneous glassy matrix the binary system $50\,BaO-50\,SiO_2$ was allowed to gel and dry to the solid state at room temperature for 6 months before being calcined as described above.

2.2 *NMR and FTIR Measurements*

^{29}Si MAS NMR experiments were performed on a Bruker CXP 300 spectrometer. All ^{29}Si MAS spectra were recorded at room temperature applying high power proton decoupling and a spinning rate of 4 kHz. Fairly short radio frequency pulses (15°–25°) and recycle delays of 30 s were used. The number of accumulated scans ranged betwen 800–2200.

Prior to Fourier transformation the FIDs have been processed by exponential multiplication using a line broadening of 30–100 Hz. In some cases proton cross polarization was employed with varying contact times (0.5–30 ms).

Table 1. Compositions of the studied gel glass systems given in mol% of the oxides.

Gel Glass Compositions	
Binary systems	$50BaO-50SiO_2$ $57TiO_2-43SiO_2$
Ternary systems	$20BaO-40TiO_2-40SiO_2$ $30BaO-40TiO_2-30SiO_2$ $40BaO-40TiO_2-20SiO_2$

FTIR spectra were measured on a BOMEM DA 8 spectrometer using the KBr pellet technique. To avoid adsorption of water, the sample cell was evacuated and the KBr dried before use. All infrared absorption spectra were recorded at room temperature in the wavenumber range from 400 to 5000 cm^{-1} with a spectral resolution of 5 cm^{-1}.

3. Results

Figures 1 and 2 represent the ^{29}Si MAS NMR spectra for samples of all systems prepared at different annealing temperatures between 60 °C and 850 °C. The spectra were decomposed into individual Gaussians in order to perform a quantitative analysis of different building units Q^n. This procedure is well-established in literature [6, 7, 9]. The Q^n nomenclature [5] describes how many oxygens n of a SiO_4 tetrahedron are interlinked to other silicon atoms ($n = 0-4$). Chemical shift assignment of single Gaussians to special groups is rather difficult in multicomponent glasses due to the large variety of possible connections Si–O–X as part of various Q^n species. In the $BaO-TiO_2-SiO_2$ gel system X can be Si, Ti, H, or instead terminal oxygen are present. As a consequence broad, featureless resonances result especially for samples annealed at intermediate temperatures. Decomposition into individual components is based in these cases on the lines of the prominent species, whose chemical shifts could clearly be assigned in the well-structured spectra of the dried gels at 60 °C and of the samples heat treated at 850 °C. The results are listed in Tables 2–5. The accuracy of the isotropic chemical shift relative to tetramethylsilane is ±0.5 to 1 ppm, that of the full width at half height (FWHH) 0.5 to 1.5 ppm and that of the relative intensity areas 2–15%.

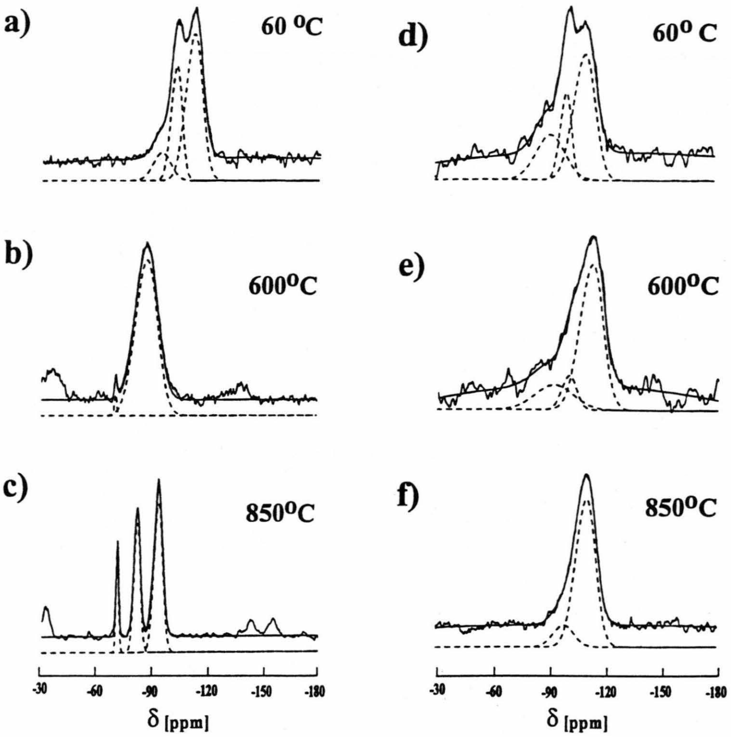

Fig. 1. ^{29}Si MAS NMR spectra of the binary gel glass systems $50BaO-50SiO_2$ (a–c) and $47TiO_2-53SiO_2$ (d–f) at different annealing stages. The closed line fitted to the experimental spectra is composed of the individual signal components given as dashed traces.

Tables 2–5. Values for the chemical shift, the full individual line width at half height and the percentage of Q^n obtained from analysis of ^{29}Si MAS NMR.

System	Annealing Temperature (°C)	Structural type	$-\delta_{iso}$ (ppm)	FWHH (ppm)	Q^n (%)
$50\,BaO-50\,SiO_2$	60	Q^4	110.7	10	57
		$Q^3(H)$	101.2	7	35
		$Q^2(H), Q^3$	92.0	8	8
	600	various	87.0	17	98
		Q^0	71.0	2	2
	850	Q^3	92.6	5	54
		Q^2	81.4	4	35
		Q^0	71.0	2	11
$57\,TiO_2-43\,SiO_2$	60	Q^4	109.5	12	55
		$Q^3(H)$	100.0	7	20
		$Q^2(2H)$	92.0	18	25
	600	Q^4	110.0	16	76
		$Q^3(H)$	100.0	7	10
		$Q^2(2H)$	90.3	16	14
	850	Q^4	109.0	12	87
		$Q^4(1Ti)$	98.0	12	13

Table 3

System	Annealing Temperature (°C)	Structural type	$-\delta_{iso}$ (ppm)	FWHH (ppm)	Q^n (%)
$40\,BaO-40\,TiO_2-20\,SiO_2$	60	Q^4	107.6	11	56
		$Q^3(H)$	99.7	7	30
		$Q^3, Q^2(2H)$	92.0	8	14
	250	Q^4	107.9	12	49
		$Q^3(H)$	100.0	8	20
		$Q^3, Q^2(2H)$	92.0	10	25
		Q^1	82.0	9	7
	275	Q^4	108.0	9	10
		$Q^3(H)$	100.0	8	20
		$Q^3, Q^2(2H)$	92.0	11	41
		Q^1	82.0	12	29
	300	Q^3	92.3	10	16
		Q^1	82.3	13	84
	500	Q^3	90.0	8	8
		Q^1	81.0	11	92
	850	Q^1	82.3	2	100.0

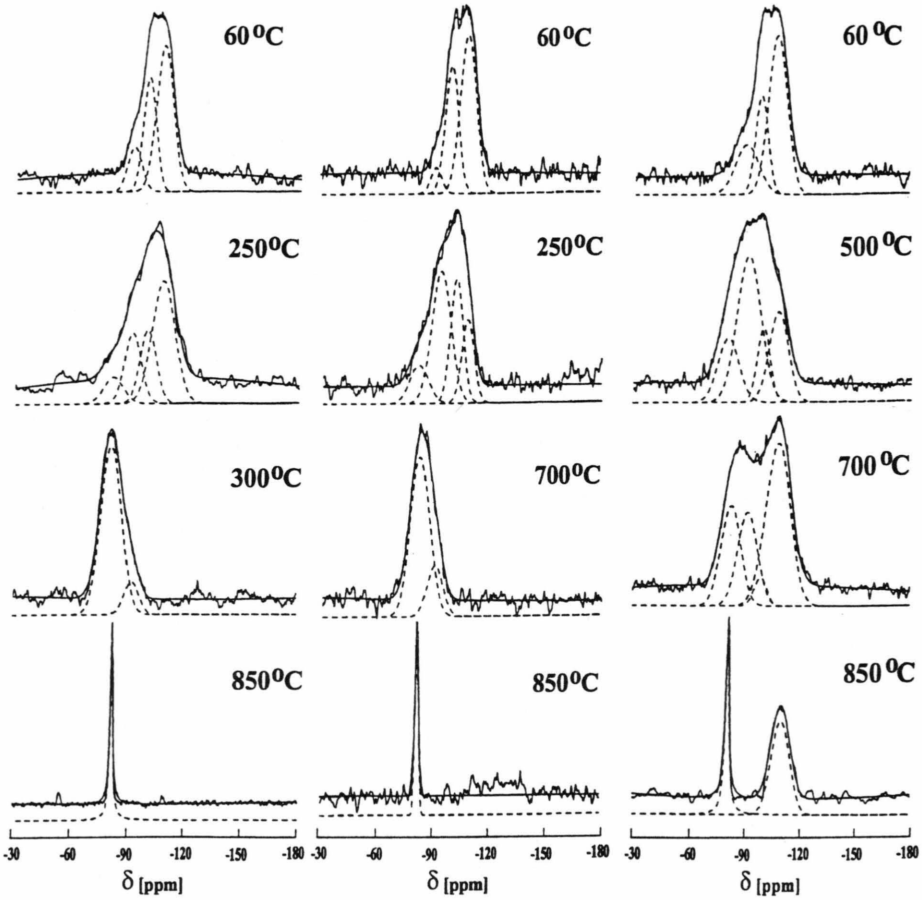

Fig. 2. ^{29}Si MAS NMR spectra of the ternary oxide system at variouis annealing stages between 60 °C and 850 °C. Compositions from left to right: $40BaO-40TiO_2-20SiO_2$, $30BaO-40TiO_2-30SiO_2$ and $20BaO-40TiO_2-40SiO_2$.

3.1 The Binary System

As limiting cases the binary systems $BaO-SiO_2$ and TiO_2-SiO_2 were of special interest, in particular to find out in which way Ba^{2+} and Ti^{4+} ions will influence the development of the silicate network during the sol-gel process. The high contents of BaO and TiO_2 have been chosen to meet the corresponding molar ratios of the oxides in the ternary composition 30 BaO–40 TiO_2–30 SiO_2. Figure 1 shows various NMR spectra at different states from the dried gels to the glasses. Table 2 summarizes all NMR derived data of both systems.

In the ^{29}Si MAS NMR spectrum of the gel, dried at 60 °C with composition 50 BaO–50 SiO_2, three different resonances could clearly be identified and assigned to a Q^4 and a Q^3 (H) (three oxygen linkages to silicon, one OH group) unit at -110.7 ppm and at -101.2 ppm, respectively. The signal of the third component at -92 ppm may arise from a Q^3 (three linkages, one O^-) as well as from a Q^2(2H) (two linkages, 2 OH groups) building element, as the silicon experiences in both polyhedra a similar chemical shift range. Cross polarization experiments show typical signal enhancements at short contact times (1 ms) for the Q^3(H) and Q^2(2H) structural types.

The sample baked at 600 °C exhibits one broad line, Fig. 1 b, with the center of gravity, δ_{CG}, at -87 ppm and a weak narrow resonance at -71 ppm, arising from Q^0 in crystalline Ba_2SiO_4 [5], present in small amounts. The wide line seems to consist of the broadened overlapping resonances of those two types of tetrahedra, whose narrow signals emerge in the spectrum of the sample annealed at 805 °C, Fig. 1 c; it has

Table 4

System	Annealing Temperature (°C)	Structural type	$-\delta_{iso}$ (ppm)	FWHH (ppm)	Q^n (%)
30 BaO–40 TiO_2–30 SiO_2	60	Q^4	108.9	10	56
		Q^3(H)	100.2	8	37
		Q^2(2H), Q^3	92.0	7	7
	250	Q^4	108.0	14	51
		Q^3(H)	100.0	10	21
		Q^3	92.0	10	21
		Q^1	82.0	11	7
	275	Q^4	108.0	12	31
		Q^3(H)	100.0	11	20
		Q^3	92.0	10	29
		Q^1	82.0	14	20
	300	Q^4	108.0	9	7
		Q^3(H)	100.0	11	11
		Q^3	92.0	14	50
		Q^1	82.0	11	32
	700	Q^3	90.0	10	21
		Q^1	82.0	12	79
	850	Q^1	82.1	2	100.0

Table 5

System	Annealing Temperature (°C)	Structural type	$-\delta_{iso}$ (ppm)	FWHH (ppm)	Q^n (%)
20 BaO–40 TiO_2–40 SiO_2	60	Q^4	108.4	12	55
		Q^3(H)	99.8	8	23
		Q^2(2H), Q^3	92.0	15	22
	300	Q^4	108.0	12	28
		Q^3(H)	100.0	8	17
		Q^2(2H), Q^3	92.0	15	51
		Q^1	81.0	6	4
	500	Q^4	108.0	13	23
		Q^3(H)	100.0	8	13
		Q^3, Q^2(2H)	91.0	15	46
		Q^1	81.0	13	18
	700	Q^4		15	48
		Q^3(H)		8	5
		Q^3		13	23
		Q^1		13	24
	800	Q^4	111.0	11	41
		Q^3	101.0	55	38
		Q^1	81.0	3	21
	850	Q^4	109.5	11	63
		Q^1	81.4	2	37

completely transformed into crystalline material. These peaks at −92.6 ppm and −81.4 ppm correspond fairly well with the isotropic chemical shifts assigned in the literature [5, 10] to Q^3 and Q^2 in crystalline $BaSi_2O_5$ and $BaSiO_3$, respectively. The presence of 50% Q^3 and 50% Q^2 leads to $\delta_{CG} = -87$ ppm, characteristic of the broad line.

Inspection of Figure 1 d reveals splittings comparable to those in Fig. 1 a in the spectrum of the system 57 TiO_2–43 SiO_2 dried at 60 °C. Cross polarization experiments have been used to support the assignment of peaks in the chemical shift range between −92 ppm and −100 ppm to Q^3(H) and Q^2(2H) units, respectively. Nevertheless small contributions of Si–O–Ti linkages cannot be excluded since they may affect the chemical shift in a similar way as an OH group [6]. In contrast to the BaO–SiO_2 composition, further annealing enhances the resonance at more negative chemical shifts (increased shielding) and results for the sample annealed at 850 °C in a predominant Q^4 fraction of 87% with a remaining rest of 13% may be Q^4(Ti) (three oxygen linkages to silicon, one to titanium) or Q^3(H).

3.2 The Ternary Systems

A selection of ^{29}Si MAS NMR spectra representative of the ternary systems are shown in Figure 2. The complete NMR results are listed in Tables 3–5. Due to observable splittings all spectra of the dried gels (60 °C) could easily be decomposed into those resonances already assigned in the binary systems and confirmed, if necessary, by crosspolarization experiments. Again, spectral contributions of Q^3 and of Si–O–Ti cross-linking are masked by the lins of Q^3(1H) and Q^2(2H), though the mixed oxide bonds give rise to weak vibrational absorptions in the FTIR spectra (Chapter 3.3).

The broad and less structured resonances of the samples annealed between 250 °C and 500 °C were composed of the aforementioned predominant lines and of an additional signal component arising at about -82 ± 1 ppm. This new peak appears in the spectra of all ternary compositions as an important or even exclusive resonance for samples heat-treated at temperatures >500 °C. With the aid of FTIR measurements it could be assigned to a silicate anion, Q^1, formed as part of the fresnoite composition, $Ba_2TiSi_2O_8$, as will be discussed later in this study. In the system 20 BaO–40 TiO_2–40 SiO_2, baked at 700 °C, a well resolved splitting indicates the beginning of a phase separation into a fresnoite like component, still amorphous, and into a SiO_2 rich region composed of Q^4 only. The glassy character of the Q^4 structure is maintained in the further calcined sam-

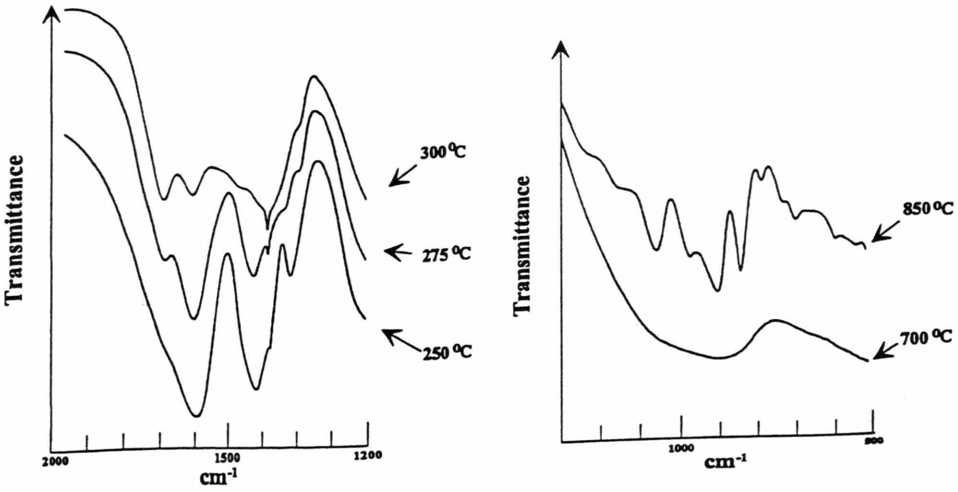

Fig. 3. FTIR spectra of the composition $30BaO{-}40TiO_2{-}30SiO_2$: a) at different annealing stages between 250° and 300 °C; b) as final gel glass baked at 700 °C and of the devitrified sample annealed at 850 °C.

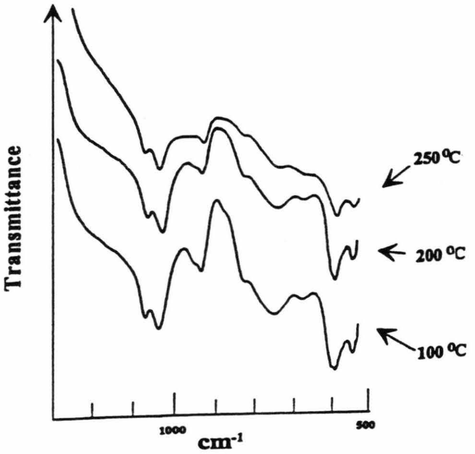

Fig. 4. FTIR spectra of the composition $40BaO{-}40TiO_2{-}20SiO_2$ annealed between 100 °C and 250 °C

ples, while the fresnoite composition transforms into the crystalline state.

3.3 FTIR Measurements

FTIR spectra have been taken preferably from the ternary systems (Figures 3–4) Typical bands at 1561 cm^{-1} and 1419 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of the carboxyl group [11] in the HAc and $BaAc_2$. These bands vanish in the medium temperature range of annealing stages at about 300 °C due to the pyrolysis of the organic rests (Figure 3 a).

Another interesting but not very intense absorption in the vibrational spectra of the dried gels appears at 945 cm^{-1}, Fig. 4, which consists of the SiOH out of plane bending vibration at ~950 cm^{-1} [12] and a Si–O–Ti component [13] at 930 cm^{-1}. At elevated annealing temperatures up to ~300 °C this band is splitted into its individual absorptions with a decreasing fraction of Si–OH vibrations. For samples calcined above 300 °C the Si–O–Ti absorption is not longer visible (not shown) since the spectrum consists only of a very broad band in this range of wavenumbers, originating from skeletal vibrations which indicate the formation of an amorphous glassy network [14].

Figure 3 b shows the FTIR spectra of two samples of the system $30BaO{-}40TiO_2{-}30SiO_2$ annealed at 700 °C and 850 °C. The first one is still glassy and exhibits featureless broad bands, whereas the crystalline sample gives rise to the specific absorptions characteristic of the silicate fresnoite [15]. Both vibrational patterns of Fig. 3 b, are the same as those reported in the literature for molten ternary $BaO{-}TiO_2{-}SiO_2$ glass of the same composition as used in our study, which had been annealed in a second step to crystallize to fresnoite [15]. Additional XRD-studies of our devitrified gel glass samples confirm the fresnoite structure.

4. Discussion

By means of ^{29}Si MAS NMR and FTIR measurements as a function of composition and annealing, detailed information about the structural development could be obtained. Regardless of the composition the ^{29}Si MAS NMR spectra of the gels dried at 60 °C are very similar. Already half of the starting TEOS material has condensed to a three-dimensional silicate network built by Q^4 and Q^3(H) units mainly. Small amounts of Si–O–Ti, though detected by FTIR measurements in the ternary systems, do not contribute essentially to the NMR spectra. However further annealing leads to very different structural evolutions depending strongly on the gel compositions.

4.1 Structural Conversion of the Binary System

In spite of the high content of BaO it has been possible to bake the $BaO-SiO_2$ gel system to the glassy state up to 600 °C. At this temperature only very small amounts of crystalline Ba_2SiO_4 were detected in the amorphous matrix. By annealing, the network-modifying Ba^{2+} cations transform the Q^4 structure of the dried gel into less condensed Q^3 and Q^2 building units in the gel-glass. Our structural interpretation is based on the findings that the chemical shift of the resonance of the glass coincides with the spectral position of the center of gravity calculated from the peaks of the devitrified sample annealed at 850 °C. It is known from literature [5, 16] that the speciation of microstructures in molten alkaline earth silicate glasses is hampered by badly resolved ^{29}Si resonances. In agreement with our results Murdoch et al. [5] showed, however, that the positions of the ^{29}Si peak maxima of the dominant species present in molten alkaline earth meta- and disilicate glasses are those found in the corresponding crystalline materials of the same composition.

An opposite structural development upon heating is observed in the TiO_2-SiO_2 gel. Polycondensation to a three-dimensional silicate network proceeds during annealing without any remarkable interlinkages to the titanium oxide structure, and this despite of the high TiO_2 content. Up to now a more pronounced hetero-condensation between these oxides has been reported only for low TiO_2 concentrations, using a two stage hydrolysis of the alkoxides in a strongly acidic medium [17]. By contrast, the preparation conditions outlined in this study are optimized to exhibit the best performance of the ternary system for the dipcoating procedure.

4.2 Evolution of the Microstructure in the Ternary $BaO-TiO_2-SiO_2$ Systems

The results of the binary systems show clearly that only Ba^{2+} acts as a modifying cation, whereas Ti^{4+} is not incorporated into the silicate structure. In all compositions of the ternary system under investigation the chemical shift of the center of gravity of the ^{29}Si resonance increases (decreased shielding) by annealing and reaches its highest value within a very narrow temperature interval of ca. 50 K between 250° and 300 °C. Within this temperature range the organic acetate ligands are pyrolized, as is mirrored in the FTIR spectra, Figure 3a. Pyrolysis releases the Ba^{2+} cations. They modify in turn the initially formed network of the dried gels. In these intermediate annealing stages the wide and nearly featureless ^{29}Si resonances reflect a broad distribution of species in the microstructure, including a certain amount of Si–O–Ti linkages. These bonds are recognized by weak vibrational absorptions, decreasing with raising curing temperatures between 60 °C and 300 °C.

By annealing, Ba^{2+} ions convert the dominant structural building units Q^4 and Q^3(H) into Q^3 and Q^1 successively. Parallel to the development of Q^1 units, parts of the titanium oxide may transform into a five-fold oxygen surrounding of a central Ti as both, Q^1 and TiO_5, are the characteristic features of a fresnoite structure [15].

The composition with the lowest SiO_2 content of 20 mol% could be baked to the glassy state till 500 °C and exhibits nearly exclusively Q^1 with only small amounts of Q^3 left. Further heat treatment devitrifies the gel glass and forms crystalline fresnoite. In agreement with [15], no Si–O–Ti absorptions are detectable in the FTIR spectra of a fresnoite like glass structure. A comparable evolution under annealing is observed in the system composed of 30 mol% SiO_2. For the silicon dioxide rich composition (40 mol%) the SiO_2 concentration exceeds that of BaO. As before, the originally formed Q^4 silicate network is partially broken into less condensed units after heat treatment up to 500 °C. At the 700 °C annealing stage, those silicate species which are not consumed by Ba^{2+} cations to form a fresnoite like microstructure, redevelop back into a silicate matrix as a separate phase. This process continues while heating and results at

850 °C in crystalline fresnoite and an amorphous Q^4 phase component as the only structural elements.

The microstructure of these special ternary gel glasses cannot be considered just as the sum of the building units identified in both binary systems. By contrast, the Ba^{2+} cations form preferably silicate dimers instead of several anions as has been found in the $BaO-SiO_2$ sample. Excess Ba^{2+}, not used for the formation of the fresnoite structure, may be incorporated into the titanate matrix. A homogeneous gel glass phase composed of all three oxides is only realized in the fresnoite part of the microstructure with a low degree of condensation, whereas remaining amounts of TiO_2 and SiO_2 develop a separate network each.

These findings deviate in some respect from former results obtained for the ternary gel-glass 65 SiO_2–20 TiO_2–15 ZrO_2 [6]. In this system polycondensation processes formed a nearly complete three-dimensioinal silicate network. In agreement with the present study no crosslinking between the oxides was detected, but by contrast none of the involved metals could act as modifying cations and thus break already formed bonds to rearrange the structure.

The authors would like to thank Prof. Dr. W. Müller-Warmuth for many fruitful discussions. Sincere thanks are due to Dr. Cornelia Cramer for the recording of FTIR spectra.

[1] G. W. Cleck and E. H. Hamilton, J. Res. Nat. Bur. Standards **57,** 317 (1956).
[2] Thesis, M.SC. Qi Chen, April 1993; Qi Chen, G. H. Frischat, and Jijian Cheng, J. Sol-Gel Sci. Technol. **2,** 535 (1994).
[3] C. J. Brinker and G. W. Scherer, Sol-Gel Science. Academic Press, Boston 1990, pp. 787.
[4] H. Eckert, Progress in Nuclear Magnetic Resonance Spectroscopy **24,** 159 (1992).
[5] G. Engelhardt and D. Michel, High Resolution Solid State NMR of Silicates and Zeolites, (Wiley, Chichester, 1988).
[6] Ch. Wies, K. Meise-Gresch, W. Müller-Warmuth, W. Beier, A. A. Göktas, and G. H. Frischat, Phys. Chem. Glasses **31,** 138 (1990).
[7] Ch. Wies, K. Meise-Gresch, W. Müller-Warmuth, W. Beier, U. Wellbrock, and G. H. Frischat, J. Non-Cryst. Solids **116,** 161 (1990).
[8] L. van Wüllen, W. Müller-Warmuth, D. Papageorgiou, and H. J. Pentinghaus, J. Non-Cryst. Solids **171,** 53 (1994).
[9] C. M. Schramm, B. H. W. S. de Jong, and V. E. Parziale, J. Amer. Ceram. Soc **106,** 4396 (1984).
[10] J. B. Murdoch, J. F. Stebbins, and I. S. E. Carmichael, Amer. Mineral. **70,** 332 (1985).
[11] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, New York 1986, 231.
[12] G. De, D. Kundu, B. Karmarker, and D. Ganguli, J. Non-Cryst. Solids **155,** 253 (1993).
[13] Y. Abe, N. Sugimoto, Y. Nagao, and T. Misono, J. Non-Cryst. Solids **104,** 164 (1988).
[14] R. J. Bell, N. F. Bird, and P. Dean, J. Phys. Chem. **1,** 299 (1968).
[15] Ch. S. Ray and D. E. Day, J. Non-Cryst. Solids **81,** 173 (1986).
[16] E. Schneider, J. F. Stebbins and A. Pines, J Non-Cryst. Solids **89,** 371 (1987).
[17] M. Schraml-Marth, K. L. Walther, A. Wokaun, B. E. Handy and A. Baiker, J. Non-Cryst. Solids **143,** 93 (1992); K. L. Walther, A. Wokaun, B. E. Handy and A. Baiker, J. Non-Cryst. Solids **134,** 47 (1991).