

^1H and ^{13}C NMR observation of the reaction of acetic acid with titanium isopropoxide

Dunbar P. Birnie III^{a,*}, Norbert J. Bendzko^b

^aDepartment of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA

^bInstitut für Neue Materialien, 66123, Saarbrücken, Germany

Received 24 July 1998; received in revised form 16 December 1998; accepted 19 December 1998

Abstract

Hydrogen and carbon NMR spectroscopy have been used to investigate the chemical modification process of titanium isopropoxide by acetic acid. The spectra confirm the belief that the titanium isopropoxide exchanges isopropyl groups with modifying acetate groups to form a molecule with approximate stoichiometry $\text{Ti}(\text{OiPr})_2(\text{OAc})_2$. This stoichiometry results even when enough acetic acid is present in solution to allow for significantly higher isopropyl replacement. In addition, progressive esterification to form isopropyl acetate results in a gradually increasing level of condensation and oxo-bridging between the Ti oligomers. Throughout the condensation process, the remaining Ti-bound acetate and isopropyl groups maintain an approximate 1 : 1 ratio, suggesting that oxo-bridge formation occurs through a transesterification process. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: NMR; Titanium alkoxide modification; Ester formation; Condensation; Acetic acid

1. Introduction

Sol–gel chemistry is an important technique for preparing chemically homogeneous coatings and powders with a variety of useful applications, as evidenced by the many conferences and symposia devoted to the topic [1–9]. Sol–gel processes usually involve various metal alkoxide molecules which are hydrolyzed under controlled conditions and then subsequently reacted to condense with each other to form metal–oxygen–metal bridging units similar to what is found in their parent oxide structures. In many cases the precursor chemicals can be very sensitive to water and therefore cannot be controllably hydrolyzed. In these cases it is desirable to make chemical modifications to the precursors to increase their stability, thus yielding more controllable chemistries during the hydrolysis and condensation steps [10–19]. Titanium isopropoxide (TIP) is one popular highly reactive alkoxide. Although many different molecules are used as modifiers, one important alternative is acetic acid [15,17,20–24].

Although rather much is known about the ability of acetate ions to modify titanium alkoxides, much remains to be learned because of the co-occurrence of the esterification reaction which gradually removes some of the modify-

ing acetate and ultimately forces precipitation of insoluble titanium-oxo-acetate species. In particular, it was desired to follow the advancement of condensation between the titanium species in solution before precipitation occurred. In addition, we sought evidence for bridging acetate moieties in solution which could indicate the incipient formation of specific known crystallization products. In the process of performing this study, we have also confirmed the conventionally accepted, nominal 1 : 2 level of acetate modification of the titanium isopropoxide precursor. Both hydrogen and carbon nuclear magnetic resonance (NMR) have been used to probe the solution chemistry and its evolution with time.

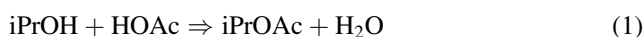
2. Background

Prior work on the use of acetic acid as a modifier to various titanium alkoxides has led to relatively good understanding of the basic processes which must be occurring. In particular, three basic steps are important: (1) exchange of isopropoxy groups with acetate groups, (2) esterification in solution resulting in gradual hydrolysis of the Ti precursors, and (3) ultimate precipitation of hexameric ring-structured titanium-oxo-acetate crystals. Each of these processes will be reviewed in turn with particular focus on questions and uncertainties which exist within this framework.

*Corresponding author.

There is uniform agreement that alkoxy groups bonded to titanium can be replaced by acetate groups in solution [12,15,17,19]. The level of modification of the TIP by acetate groups is quite important because the alkoxy groups are known to be much more rapidly attacked by water in comparison to acetate groups (thus the benefit of using it as a modifier) [10,18,20–22]. In most cases, the level of modification by acetate groups has been reported to saturate at two per titanium atom. However, occasional literature reports have shown higher modification levels [25–28] depending on which alkoxide is being used and the conditions of study (for example, modification up to a level of 3 appear to be possible if the starting reactant is acetic anhydride rather than acetic acid). Also, replacement levels higher than 2 often result in an oxolated dimeric molecular unit.

The second important process is the esterification reaction which results in the production of water [15,21,24–26,29–31]. One of the byproducts of the acetate replacement of isopropyl groups (described above) will be isopropanol. The direct esterification reaction between this isopropanol and acetic acid can be written as



Water produced according to reaction (1) will be able to hydrolyze Ti-bound isopropyl groups leaving terminal hydroxy groups which can condense forming Ti–O–Ti bridges. It has also been pointed out that a direct ‘transesterification’ can also occur [15,29]. In this case, titanium bonded isopropyl and acetate ligands can participate in a direct condensation reaction, also yielding isopropyl acetate as a byproduct along with the Ti–O–Ti condensed bridge. Related reactions can also occur between free acetic acid and bound isopropyl groups or free alcohol and bound acetate. Whatever the true reaction mechanism, all possible combinations of ester production will ultimately create oxygen linkages between titanium atoms, even if only through the subsequent rapid reaction of the water. No matter which reaction pathway is fastest, there will be only one Ti–O–Ti bridge formed for every ester molecule formed.

It has also been pointed out that the esterification reaction provides an homogeneous method for gradually introducing water into a system, in contrast to physical intermixing which gives a broad range of chemical mixing levels [31]. Because of the importance of the esterification reaction, its evolution with time was another focus of the present work.

As ester molecules gradually form in these HOAc + TIP mixtures the titanium-oxygen network gradually increases in complexity until ultimately precipitation occurs. Although the present research is focused on the processes which occur in the solution, it is instructive to review the structures and bonding arrangements found in these precipitates since similar arrangements are expected for molecules in solution.

Several studies of crystallization products which form from acetic acid modified titanium alkoxide solutions have been reported [15,30,32–35]. In every case the product

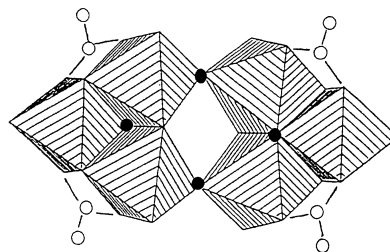


Fig. 1. Titanium oxo-bonded ring hexamer molecule found in 1 : 1 TIP : HOAc solutions after aging. Open circles show positions of carbon atoms in bridging bidentate acetate groups. Filled circles show positions of bridging oxygen atoms. Figure adapted from reference [33].

which crystallizes is a Ti hexamer ring structure. The arrangement of the ligands and the interconnection between the Ti octahedra depends on the amount of HOAc provided for the reaction as well as the nature of the alkoxy group being used. Fig. 1 shows the hexamer which forms in 1 : 1 mixtures of TIP and HOAc [33]. Bidentate bridging acetate groups are shown as stick figure molecules around the periphery. A reaction sequence was proposed where the hexamer rings formed by connecting a pair of trimer units together [15]. The composition of the resultant hexamer was found to be $\text{Ti}_6\text{O}_4(\text{OiPr})_{12}(\text{OAc})_4$. The four bridging oxo atoms are indicated by filled circles in the figure. Two of these oxo bridges are shared three ways while two are shared between only two titanium octahedra.

As pointed out in Ref. [32], the occurrence of this molecule is not fully explained since the starting 1 : 1 mixture of HOAc + TIP would not have enough acetate to convert all titaniums into these hexamers: each of the four oxo-bridges arises through the formation of an isopropyl acetate molecule. Therefore each ring with six titaniums will acquire eight acetate groups for its formation. This clearly indicates that a significant number of less-reacted Ti units are still left in solution from which the crystals were grown.

Crystals which form from 1 : 2 mixtures of TIP and HOAc were found to be a related hexamer ring structure: $\text{Ti}_6\text{O}_4(\text{OiPr})_8(\text{OAc})_8$ [32,34]. It was also similar to the molecule found for titanium butoxide/HOAc reactions at the same level [33]. The structure of this molecule is shown in Fig. 2, where the oxo atoms are again shown as filled circles. Note that now the hexamer is better described as being formed from dimer and monomers with more frequent bidentate bridging acetate groups. However, there are again two each of the two-way and three-way shared oxo atoms in each hexamer in a similar arrangement as found in the first molecule. A nearly identical structure formed for titanium ethoxide-HOAc solutions [35], even though the available acetic acid in solution was nearly twice as concentrated as what was used in the isopropoxide work. Finally, another similar hexamer ring structure was formed for methacrylate modified titanium ethoxide [36]. So it can be seen that these hexamer ring units are quite common alkoxide/carboxylate reaction products.

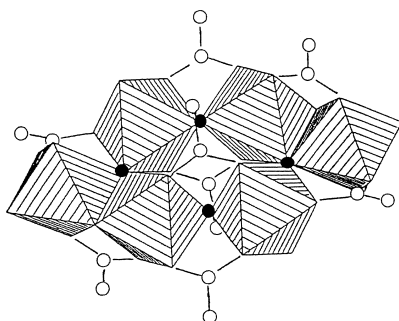


Fig. 2. Titanium oxo-bonded ring hexamer molecule found in 1 : 2 TIP : HOAc solutions after aging. Open circles show positions of carbon atoms in bridging bidentate acetate groups. Filled circles show positions of bridging oxygen atoms. Figure adapted from reference [33].

The rather broad similarities between these various hexamers are worth noting. They all have octahedral coordination of the titanium atoms. Acetate groups form bidentate structures that form bridging connections between the titanium octahedra. These must represent substantially stable conformations and bonding situations in these and related systems.

For future comparison with the present NMR solution measurements, all of the above hexamer ring structures are found to have an (oxo-bridge) to (titanium atom) ratio, O/Ti , of 0.666. In later discussions, the O/Ti ratio will be used as a measure of the relative level and density of condensation in the solution, on average.

The various reports of different levels of modifier substitution and the relative lack of investigation of titanium isopropoxide at potential acetate modifications levels higher than 2 motivated the present work. In addition we sought information about the development of the esterification reaction and how it relates to the evolution of precursor structure in the TIP–acetic acid system.

3. Experimental procedure

The present work has focused on solutions with two different ratios of TIP : acetic acid 1 : 2 and 1 : 4. This compliments prior investigations in several ways. This extends our view beyond the 1 : 1 level examined by Sanchez et al. [15], it studies the 1 : 2 level which is normally thought of as the maximum modification level, and it examines the 1 : 4 level used at an early stage of the ‘inverted-mixing-order’ chemistry presented by Assink and Schwartz [25]. In addition to these modifier additions, other solutions were investigated in relation to the ester formation reaction. We examined mixtures of acetic acid with isopropanol, water with acetic acid, water with isopropanol, and neat solutions of all precursor to help determine the characteristics of peak positions, chemical group identifications, and chemical shifts.

1H and ^{13}C NMR spectra were taken on a Bruker AC200 spectrometer. Deuterated chloroform was used as a lock

substance and tetramethylsilane was used to reference peak locations. All samples were prepared under Ar to prevent atmospheric water from entering and were measured at room temperature.

4. Results

Table 1 gives a summary of the 1H NMR spectrum peak positions for pure substances of precursors measured in this study. The solvent mixtures described above showed significant chemical shift differences which depended on acid content of the solution, as shown in Tables 2 and 3. No distinct peaks for isopropyl acetate ester were observed in our isopropanol–acetic acid mixtures. While most peaks were relatively fixed in position, the acidic proton peak (which combined alcoholic protons or water as well) shifted dramatically, depending on the nature of the solution being measured. Note, that a separate measurement of a 8 : 1, alcohol : water solution, gave distinct peaks for both alcoholic proton and water (at 5.04 and 4.24 ppm, respectively). So the peak shift, which is due to rapid exchange, is primarily mediated by the acetic acid molecules.

Table 1
Reference peak identifications for pure substances using 1H NMR

Molecule	Resonating atom in molecule	Peak position
Titanium isopropoxide	$Ti(OCH(CH_3)_2)_4$	1.24 (D)
	$Ti(OCH(CH_3)_2)_4$	4.50 (H)
Isopropanol	$(CH_3)_2CHOH$	1.13 (D)
	$(CH_3)_2CHOH$	3.96 (H)
	$(CH_3)_2CHOH$	4.93 (S)
Acetic acid	CH_3COOH	2.04 (S)
	CH_3COOH	11.73 (S)
Water	H_2O	4.78 (S)

S = singlet, D = doublet, and H = heptet.

Table 2
Reference peak observations for isopropanol–acetic acid mixtures. Only the acidic/alcoholic proton peak is found to shift significantly with the solution chemistry

Isopropanol : acetic acid mixing ratio	1 : 0	4 : 1	1 : 1	1 : 4	0 : 1
Methyl groups (isopropyl)	1.13	1.16	1.16	1.18	–
Methyl groups (acetate)	–	2.01	2.06	2.06	2.04
Central H (isopropyl)	3.96	3.99	4.07	4.06	–
Combined acidic and alcoholic protons	4.93	6.12	8.16	10.19	11.73

Table 3
Reference peak observations for water–acetic acid mixtures. Only the acidic-water proton peak is found to shift significantly with solution chemistry

Water : acetic acid mixing ratio	1 : 0	1 : 1	1 : 8	0 : 1
Methyl groups (aceto)	–	2.07	2.07	2.04
Combined water and acidic protons	4.78	8.00	10.18	11.73

Table 4

Reference peak identifications from ^{13}C NMR. Isopropyl acetate peak locations from trace amount appearing in 1 : 1 acetic acid/isopropanol mixture

Molecule	Resonating atom in molecule	Peak position
Titanium isopropoxide	$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$	76.2
	$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$	26.6
Isopropanol	$(\text{CH}_3)_2\text{CHOH}$	63.7
	$(\text{CH}_3)_2\text{CHOH}$	25.3
Acetic acid	CH_3COOH	178.6
	CH_3COOH	20.8
1 : 1 acid/alcohol	CH_3COOH	175.8
	$(\text{CH}_3)_2\text{CHOH}$	64.6
	$(\text{CH}_3)_2\text{CHOH}$	24.9
	CH_3COOH	20.8
Isopropyl acetate	$(\text{CH}_3)_2\text{CHO}_2\text{CCH}_3$	172.0
	$(\text{CH}_3)_2\text{CHO}_2\text{CCH}_3$	68.4
	$(\text{CH}_3)_2\text{CHO}_2\text{CCH}_3$	Hidden by iPrOH
	$(\text{CH}_3)_2\text{CHO}_2\text{CCH}_3$	21.8

Table 4 gives the data for the ^{13}C NMR spectra of reference samples. The ^{13}C NMR spectrum of the 1 : 1 alcohol + acid mixture showed (barely) the presence of the isopropyl acetate ester which formed the esterification reaction given above as Eq. (1). Peak integration showed that less than 1% formed in this 1 : 1 solution, even though it was left stirring at room temperature overnight before

examination. (The low concentration explains why no peak was observed in the ^1H NMR spectra discussed above in Table 2.) All of these peak positions and assignments are consistent with those presented in an earlier study [25].

The full ^{13}C and ^1H NMR spectra for the acetic acid modified TIP solutions are given in Figs. 3 and 4, respectively. In these (and all subsequent) figures the 1 : 2 mixture is positioned directly above the 1 : 4 mixture to facilitate comparison between spectra. Both solutions were made on the day of NMR analysis and were examined within a few hours after synthesis. Distinct and meaningful changes can be observed in three regions of the ^{13}C NMR spectrum, as well as in part of the ^1H NMR spectrum. Each of these detailed changes in the spectra and their inferred meaning with respect to the chemistry are discussed below.

The sharp peaks which appear in Fig. 3 near 171, 68, and 21.8 show a strong presence of isopropyl acetate. Peak integrals allow an estimate of approximately 6% of the isopropyl groups have reacted to form ester. Other interesting features in the carbon spectrum are better identified on expanded scales. Fig. 5 shows the methyl region of the carbon spectrum (21–26 ppm). The sharp peak at 21.8 ppm in each sample arises from the two methyl groups in the isopropyl ligand of the isopropyl acetate ester. The peak has not shifted measurably from the position found in the reference mixture reacting acetic acid and isopropyl alcohol. Interestingly, there is another sharp peak just to the right

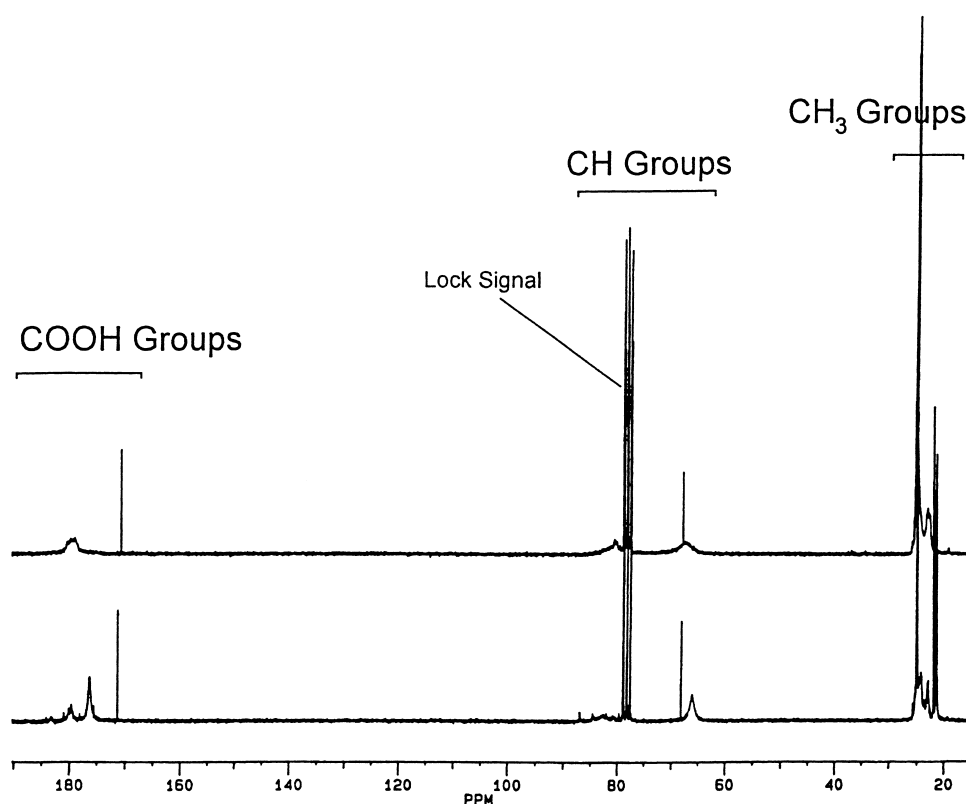


Fig. 3. ^{13}C NMR spectra for TIP modified by acetic acid at levels of 1 : 2 (above) and 1 : 4 (below).

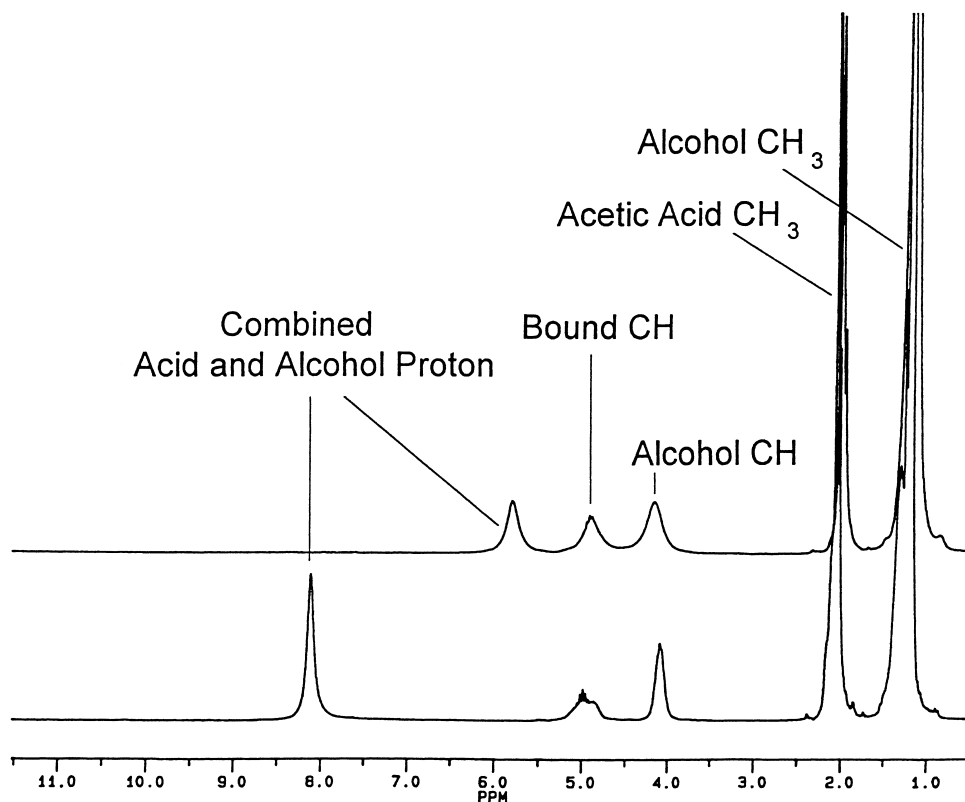


Fig. 4. ^1H NMR spectra for TIP modified by acetic acid at levels of 1 : 2 (above) and 1 : 4 (below).

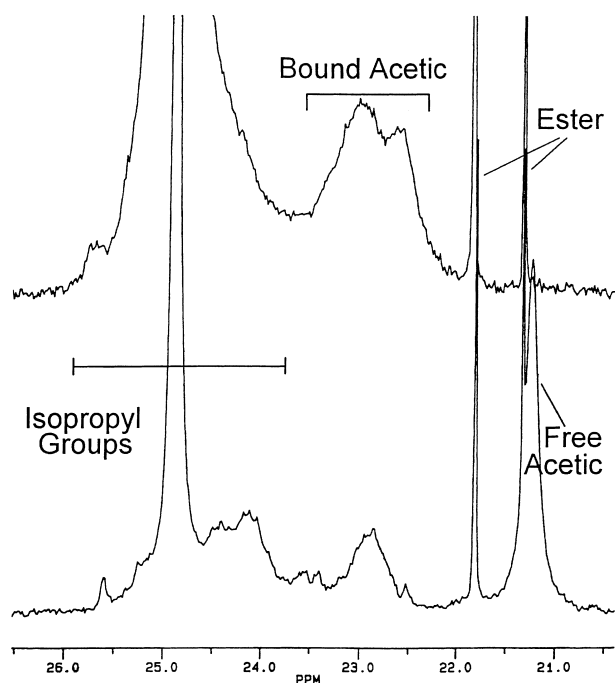


Fig. 5. Detail of the ^{13}C NMR spectra for TIP modified by acetic acid at levels of 1 : 2 (above) and 1 : 4 (below).

at 21.3 ppm. This peak appears by itself in the 1 : 2 sample (upper spectrum), but is merged with another broader resonance in the 1 : 4 sample (lower spectrum). Peak integration for the 1 : 2 sample finds an area that is half as large as the peak at 21.8 suggesting that this derives from the methyl group in the acetate part of the ester molecules. The broader overlay in the 1 : 4 mixture is in a position which is consistent with methyl groups in free acetic acid. Together these indicate that *when TIP and acetic acid are mixed together at a ratio of 1:2 there is no observable free acetic acid left after the reaction*, while when they are mixed in a ratio of 1 : 4 then significant free acetic acid is left in solution.

Fig. 5 has other interesting features. In the 1 : 2 solution (upper spectrum), there are two other large peaks. If we break peak integration at the minimum point between the two peaks, then the two peak areas are in a ratio of 4 : 1. This is consistent with the left peak coming from all methyl carbons in other (non-ester) isopropyl groups and the right peak coming from all methyl carbons in (non-ester) acetate groups. Because we know that the acetic acid is modifying the TIP, and because no free acetic acid was observed, then we infer that the smaller peak (from 22.0 to 23.5) is from acetate groups bonded directly to titanium. No direct infor-

mation is available about the specific coordination or location of these groups, but its rather complex character suggests that acetate groups are found in more than one configuration. This is compatible with the result of the esterification reaction, as discussed further below.

The arrangement of the peaks in the methyl region of the spectrum is much more complicated for the 1 : 4 mixture (Fig. 5, lower spectrum). It shows a clear peak identified above as the bound acetate in the 22.0–23.5 ppm region. If we break peak integration at the same location as used for the 1 : 2 ratio sample and then compare it with the integrated area of the free acetic acid peak (at 21.2 ppm), we find that about 40% of the acetate groups are bound to titanium. The remaining 60% includes both free acetic acid and ester molecules. This indicates that from the four original acetate groups, somewhat fewer than two have bonded with TIP and the remainder have stayed in solution as free acetic acid and ester molecules. The peak in the 24 to 26 ppm region is a result of both free and bound isopropyl groups, however it was not possible to differentiate them because the peaks were too close together. In addition, the 1 : 4 sample (lower spectrum) had evidence for more than one distinct bonding environment for the bound isopropyl groups.

Close inspection of the far left of Fig. 3 (in the 170 to 185 ppm region) also supports the above findings. Fig. 6 shows an expansion of this range. The acetate group from the ester shows up with a sharp peak near 171 ppm. On the top spectrum (for the 1 : 2 mixture), the broad peak between

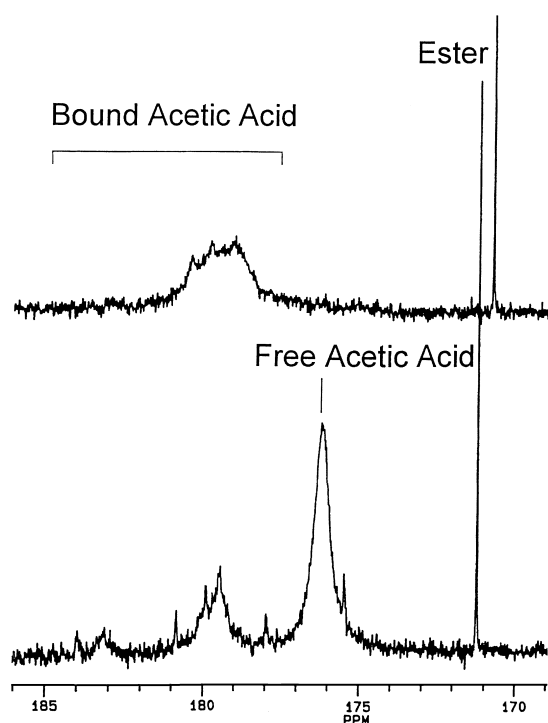


Fig. 6. Carboxylic region of the ^{13}C NMR spectra for TIP modified by acetic acid at levels of 1 : 2 (above) and 1 : 4 (below).

178 and 181 ppm can then be associated with acetate ligands bound directly to titanium. This shows up as a clearly identifiable peak in the 1 : 4 solution (lower spectrum). In the 1 : 4 solution there is an additional stronger peak near 176 ppm which closely matches the peak position of acetate groups in the 1 : 1 acetic acid+isopropanol reference mixture so it can be assigned to free acetic acid. There is evidence of another peak near 183 ppm, suggesting that yet a third distinct bonding environments exists in this solution. This could be from acetate groups bonded directly to titanium, but in another configuration. If we integrate the entire range of bound acetate groups (from 178 and 185 ppm) and compare this with the integral of the free acetic acid peak (from 174 to 177 ppm) and the ester (at 171 ppm), we find them occurring at 34%, 60%, and 6%, respectively. Note that since the spectrum for the 1 : 2 mixture displays no observable free acetic acid peak, all non-ester acetate is bound to Ti (94%).

Next, in the central region of the ^{13}C NMR, expanded as Fig. 7, there is further evidence to support the partial replacement of isopropyl groups by acetate groups in these solutions. The closely spaced triplet near 78 ppm in both upper and lower plots derives from the chloroform used as the block substance. The presence of the isopropyl acetate in both samples is shown by the sharp line near 68 ppm. In the 1 : 2 ratio sample (upper spectrum), there are two broad peaks which can be associated with isopropyl groups in two different configurations. The smoother character of the peak on the right, and its position compared to the reference samples indicates that this belongs to free isopropanol. So, the peak at the left can be attributed to isopropyl groups bonded to titanium. A similar peak assignment applies to the lower spectrum, though more structure is apparent in the bound isopropyl group region. Peak integration allows for estimation of the distribution of isopropyl groups between the three configurations (but only semi-quantitatively since the chloroform lines overlap with the edge of the bound isopropyl peak). In the 1 : 2 mixture, the bound: free: ester proportions are about 40 : 56 : 4, while for the 1 : 4 mixture they are about 36 : 56 : 8. Note that the position of the chloroform would tend to cause a relative underestimate of the bound isopropyl fraction. Again, this region of the spectrum supports the conclusion that the level of acetate modification of TIP is nearly two.

Now, referring back to Fig. 4, the effects of modifier addition can be observed in the ^1H NMR spectra. The primary difference in the spectra is that the furthest peak to the left has shifted significantly, while the remaining four peaks have stayed relatively fixed. This suggests that this left-most peak be matched with the acidic proton (see Table 2 showing the strong shift in acetic acid/isopropanol mixtures). Peak integration supports this assignment. The two peaks near 5.0 and 4.1 are each too small to separately account for all of the isopropyl groups in solution. In fact, the sum of intensity in both peaks together accounts exactly for all isopropyls. As with the ^{13}C analysis above, this

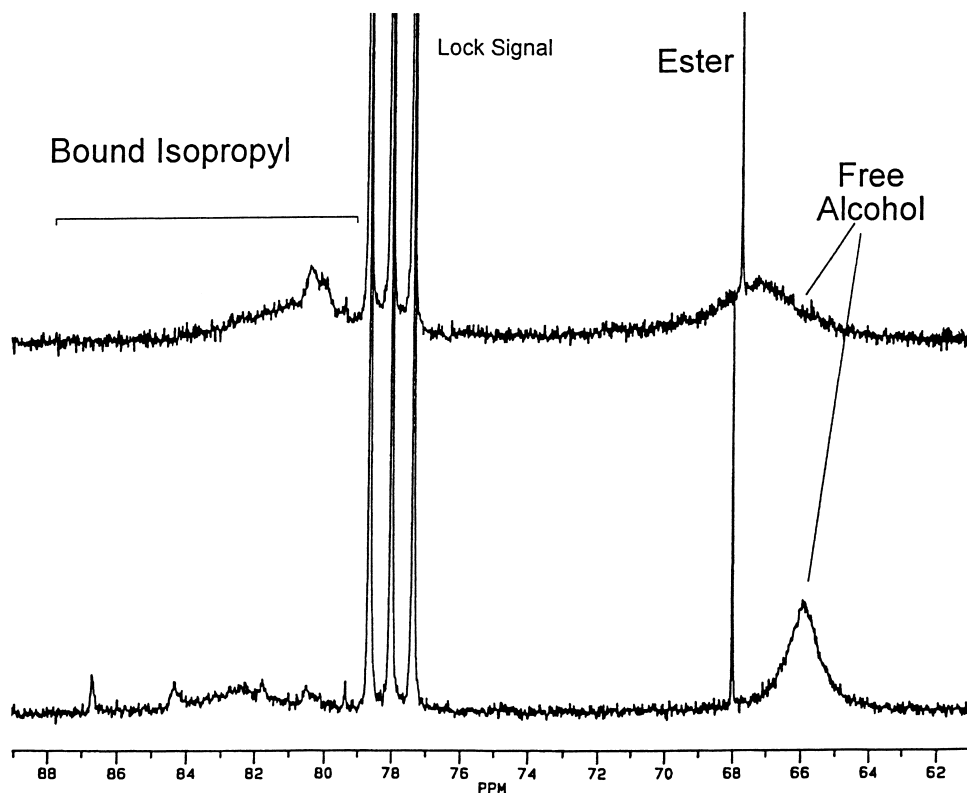


Fig. 7. Expansion of the ^{13}C NMR spectra for TIP modified by acetic acid at levels of 1 : 2 (above) and 1 : 4 (below).

indicates that the isopropyls are found in two distinctly different bonding configurations. The reference data in Table 2 show that the isopropyl resonance found in this region shifts only slightly between samples, suggesting that the peak near 4.1 is associated with free isopropyl alcohol. The possibility that the other peak is only from isopropyl groups in ester molecules can be ruled out because not enough of the ester has formed (see above results). The peak integrals indicate that 58% of the isopropyl groups are in isopropanol, while 42% are bound isopropyl groups. The 1 : 2 mixture shows a 57 : 43 distribution between the same two peaks.

The strong shift of the acidic/alcoholic proton peak can be used as a further probe of the solution chemistry. Examination of the shifts observed for the reference solutions (given in Table 2) shows that the peak shift is nearly linear with the molar concentration of acetic acid in solution. If this relationship were to remain reasonably similar for the more complex solutions studied here, then the peak positions would suggest that the 1 : 2 solution had very little acetic acid in solution, while the 1 : 4 solution had a mixture of about 1 : 1 of HOAc : iPrOH. This is exactly what would result if acetic acid exchanged with only two of the four isopropyl groups to modify the TIP, resulting in two free isopropanol molecules in solution. Thus, these peak shifts are in quantitative support of the scheme developed by examination of the ^{13}C NMR above.

We have also monitored the time evolution of the esterification reaction by examining the 1 : 4 solution in three different conditions, as-mixed, after 1 day, and after 2 days. Within 3 to 5 days, solutions of this stoichiometry consistently start to gel or precipitate, indicating the formation of a strong network of condensed Ti–O–Ti connections. We can measure the progress of the ester production by using the prominent ester peaks discussed above. Table 5 shows the estimated percent of acetate groups which have reacted to form ester molecules, as a function of time. They clearly indicate that the esterification reaction is advancing with time. By comparison with the simple mixture of isopropyl alcohol and acetic acid (1 : 1) used for a reference solution (where less than 1% ester formed), the significantly larger

Table 5

Evolution of solution chemistry with time in various TIP : acetic acid solutions. Data are provided for: solution age, ester content (averaged from methyl and carboxyl region integrals), calculated O/Ti ratio, and measured Ti-bound ligand fractions (OAc based on carboxyl C NMR, OiPr based on methine H NMR)

TIP : HOAc ratio	1 : 2	1 : 4	1 : 4	1 : 4	1 : 4
Age (hours)	6.5	5	20	25	48
Ester content (as % of all acetate)	6.0	6.1	7.2	9.0	11.8
Resulting O/Ti	0.12	0.24	0.29	0.36	0.47
% OAc bonded to Ti	94	34	40	37	37
% OiPr bonded to Ti	43	42	39	44	37

amounts of ester in the alkoxide mixtures tend to support the suggestion that most of the ester occurs through a ‘trans-esterification’ reaction rather than a direct esterification reaction. Or, it could indicate that the direct esterification reaction was accelerated or catalyzed by titanium species acting as Lewis acids.

As mentioned in the background section, the ester concentration in solution is a direct measure of Ti–O–Ti bridge formation. Since the ester quantities in Table 5 are referenced to the total acetate addition, the average O/Ti ratio for each solution is found by multiplying the percent of ester by either 2 or 4, depending on the level of HOAc added to the mixture. This deduced O/Ti ratio is also presented in Table 5. For the 1 : 2 sample, the average O/Ti ratio was 0.12 (after 6.5 h of reaction), while for the 1 : 4 mixture, the O/Ti ratio increased gradually from 0.24 after 5 h of reaction to 0.47 after 48 h of reaction. All of these values are smaller than the 0.666 ratio which would be found in the crystalline hexamer units.

Finally, Table 5 also includes quantities of bound acetate and isopropyl groups deduced from the NMR peak integration. It can be seen that throughout the reaction the amounts of bound acetate and bound isopropyl are very close. This holds true for all 1 : 4 sample times as well as for the 1 : 2 sample (this is best recognized by following the bound isopropyl content because both acetic acid modification levels had the same starting OiPr count).

5. Discussion

The results presented above have demonstrated two key effects caused by the addition of acetic acid to TIP. First, the acetic acid modified the TIP by substituting some acetate groups for isopropyl groups. And, second, the acetic acid drives an esterification reaction which advances gradually with time. It is interesting to discuss some of the implications of these findings, especially with respect to the state of bonding or polymerization of the titanium oligomers, and also with respect to the effect this might have on subsequent hydrolysis and condensation reactions that are of importance to various sol–gel syntheses.

The assessment of bound versus free acetate or isopropyl groups given above must account for all groups present in the two types of solution measured. Since the modification reaction is thought to be a simple replacement of an isopropyl group by an acetate group, then we would expect that the estimated percentages of bound isopropyl and bound acetate groups should sum to 100% for the 1 : 4 mixture of TIP and acetic acid. The two estimates of isopropyl group bonding to titanium made above were 36% and 42%, while the two estimates of the acetate group binding were 34% and 40%. The fact that this sums to less than 100% is compatible with the co-occurrence of the esterification reaction because each ester molecule formed actually removes *two* titanium bonding sites from use by either acetate or isopropyl group

attachment. In addition, the peak integrals must be considered as a semiquantitative estimate, probably accurate only at the level of a few percent or so. Another complicating factor is that we cannot identify a specific isopropyl-related ^1H NMR peak from the ester. It is likely that this is included in the bound OiPr quantities listed in Table 5. So within the accuracy available to us, it is only possible to say that the level of acetate group attachment is approximately the same as isopropyl group attachment and that this approximate equality holds true *throughout solution aging*. It should also be noted that no observable quantity of free acetic acid was found in the 1 : 2 mixture (upper spectra, Figs. 5 and 6). Together, these factors suggest that the acetate modification of TIP results in a molecule close to this stoichiometry: $\text{Ti}(\text{OiPr})_2(\text{OAc})_2$, but that modification does not extend beyond this level in the 1 : 4 solution. As condensation of these molecules progresses, the average titanium bonding environment can be described by the following composition: $\text{TiO}_R(\text{OiR})_{2-R}(\text{OAc})_{2-R}$, where R is the deduced O/Ti ratio for the solution.

The initial condition of the TIP solution before modification has been characterized previously [37,38]. It was determined that monomers are the preferred arrangement of pure titanium isopropoxide. This was attributed to steric hindrances provided by the branched isopropyl group. Acetate groups are well known to be able to form a variety of different coordination modes with titanium, including bidentate and other configurations [12,15,21,30], so we might expect this to occur in this case too. A bidentate chelating configuration can allow for titanium to shift from four-fold to six-fold coordination in solution. It is interesting to consider that the $\text{Ti}(\text{OiPr})_2(\text{OAc})_2$ stoichiometry would have exactly six coordinating oxygens if both acetate groups were in bidentate configurations and the molecule remained monomeric. However, the tendency for various alkoxide molecules to aggregate into dimers or trimers [12,15,17,30,37,38] prevents us from being completely certain about the structure of the acid modified TIP.

The occurrence of the esterification reaction forces rather drastic modifications to the structures found in solution. Each ester molecule formed produces a Ti–O–Ti bonding unit. This is true even if the direct esterification reaction (Eq. (1)) is the principal route, because the water would rapidly hydrolyze an isopropyl group, which would ultimately lead to condensation of Ti–OH groups. As more ester molecules are formed then the frequency of diatomic oligomer units increases. Eventually longer chain units can be built, until the solution gels. As mentioned above, this occurs in three to five days, depending on temperature. The breadth of the NMR peaks of our solution samples provides evidence for this gradually evolving solution structure; if a direct reaction to form hexamer units occurred then we would expect much sharper peaks like those that were found when butoxy-based hexamer crystals were redissolved back into solution [30]. Thus our data are evidence for a much more complicated solution structure.

It is interesting to consider the structure consequences of the gradually increasing level of oxo-bridge formation (as indicated by the rising O/Ti ratio with time). As a starting point we acknowledge that the hexamer molecules must certainly form after long enough times (as evidenced by the appearance of these crystals). However, we believe that it is very unlikely that these hexamers are the first reaction product to arise from the acetate modified TIP molecules. Instead, there must be a gradual evolution that occurs in the solution resulting in a *distribution* of Ti unit sizes, where this distribution of sizes evolves with time as the esterification reaction progresses.

Because of steric hinderances imposed by the bulky isopropyl groups, the starting configuration for the TIP molecules is known to be monomeric. And, as discussed above, it is possible that the di-modified titanium species might remain monomeric, but has achieved a more favorable octahedral coordination by the addition of the bidentate acetate groups. Since esterification is gradual, the initial condition of the solution will be almost completely dominated by these monomers. Then dimer formation will likely occur only when two monomers condense giving an oxo-bridge between them. If this occurred then the following molecule would result: $\text{Ti}_2\text{O}(\text{OiPr})_3(\text{OAc})_3$. This molecule has an O/Ti ratio of 0.5. The creation of a trimer could happen without oxolation (since three-way-shared oxo atoms are present in the hexamer rings) and would result in $\text{Ti}_3\text{O}(\text{OiPr})_5(\text{OAc})_5$ formation, where this molecule has an O/Ti ratio of 0.333. Note that this does not indicate any overall change in average value of the O/Ti ratio in solution since the monomer (having O/Ti = 0.0) that reacted with the dimer to form the trimer would have already been present in the solution. According to a model presented earlier [15], trimers react together to form the hexamer rings. The proposed reaction sequence involved hydrolysis and then condensation of the resulting Ti–OH groups. However our measurements of the esterification reaction in NMR standard solutions showed that the water generation rate following reaction (1) alone was too slow to yield the ester concentrations observed in our NMR of the TIP + HOAc mixtures. And, it should be noted that before a hexamer ring unit can be completely formed there must be *two* new oxo-bridges created between the two trimers that are being connected. Thus, we suggest that an intermediate state may occur where the two trimers are attached by only a single new oxo-bridge. This molecule, with composition $\text{Ti}_6\text{O}_3(\text{OiPr})_9(\text{OAc})_9$, would have an O/Ti ratio of 0.500. When the additional ester molecule was able to react out, then the final hexamer unit (having O/Ti = 0.666) would form: $\text{Ti}_6\text{O}_4(\text{OiPr})_8(\text{OAc})_8$. In any case, the development of significant quantities of the hexamer units in solution must follow a reaction path where intermediates with a variety of configurations are found. These would give various NMR signatures and would explain the breadth of some of the peaks, as discussed above.

The present measurements of the average O/Ti ratio in various solutions (shown in Table 5) are compatible with the above description of solution shows an average O/Ti value of only 0.12 after about 6.5 h of reaction, indicating that most species are still monomers at this time, but that some of these have reacted forward into more oxolated species. For the 1 : 4 solution, the earliest O/Ti value is 0.24, which could result from a mixture of monomers and dimers (and/or trimers). With longer reaction time the O/Ti number rises so that after 48 h that total solution average is nearly 0.5. It is likely that these solutions are made up of a broad spectrum of molecule sizes, with a significant fraction that are either open or closed ring hexamer structures.

As mentioned above, the measured peak intensities for bound OiPr and OAc indicate that the proportion of these bound ligands stays at a relative level of 1 : 1 throughout the aging of the 1 : 4 solution. This argues in favor of transesterification between adjacent or nearby Ti-bonded OAc and OiPr groups as the main condensation pathway for network formation. If ester formed via free HOAc attack of bound OiPr groups (or the reverse), then it might be expected that a noticeable imbalance in ligand attachment could develop, especially at longer times when more ester had formed. The continual 1 : 1 ligand ratio throughout the reaction supports the general framework presented above because the stoichiometries of all molecules presented here in the discussion have this ratio as well.

The presence of two isopropyl groups attached to each titanium after acetate modification could have certain advantages during sol–gel syntheses. In these processes, intentional hydrolysis and condensation reactions will be caused by addition of water to the solution. These additions will usually be made much earlier than the time frame investigated in the present NMR investigations, suggesting that even less ester formation (and therefore less oxo-bridge formation) will have occurred. Thus the externally introduced water will be reacting primarily with the di-modified monomer species. It is well known that the isopropyl groups are much more reactive with water in comparison to acetate groups or other modifiers [10,18,20–22]. In this case, if only two rapidly reacting groups are available, then we might project that a linear chain configuration could occur with acetate side groups being slowly attacked by other waters to build a three-dimensional network. However, with the first rapid step occurring at two sites only, then the condensation process would be much more controlled.

It is interesting that the earlier NMR study of post-hydrolysis solutions [25] found that only acetate groups were left bonded into the Ti network. This is compatible with the present findings and supports the suggestion that the hydrolysis *does* preferentially attack the isopropyl groups. The present work, which has focused on *pre*-hydrolysis solutions, has shown how the acetic acid modifies the TIP in the earliest stages of solution formation. This allows us to better understand how the precursors react with each other to build a network and ultimately form particles or gels.

6. Conclusions

Carbon and hydrogen NMR measurements have been made of titanium isopropoxide–acetic acid mixtures of two mixing ratios. Careful examination of the spectra for 1 : 2 and 1 : 4 mixtures has verified that acetate groups replace isopropyl groups up to a stoichiometry of approximately $\text{Ti}(\text{OiPr})_2(\text{OAc})_2$. Only two isopropyl groups are replaced even if there are four acetate groups present in the solution. In addition, the esterification reaction was monitored showing that longer reaction times resulted in larger concentrations of the ester. A direct byproduct of this ester formation is an increase in Ti–O–Ti bonding which ultimately leads to gelation or crystallization. The TIP modification process by acetic acid offers particular advantages during controlled hydrolysis and condensation in solution.

Acknowledgements

The principal author is greatly appreciative to H. Schmidt and R. Naß for supporting his sabbatical at the Institute for New Materials in Saarbrücken Germany where the entirety of this work was carried out.

References

- [1] Better Ceramics Through Chemistry, C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), MRS Symp. Proc., vol. 32, 1984.
- [2] Better Ceramics Through Chemistry II, C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), MRS Symp. Proc., vol. 73, 1986.
- [3] Ultrastructure Processing of Advanced Ceramics, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, New York 1988.
- [4] Better Ceramics Through Chemistry III, C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), MRS Symp. Proc., vol. 121, 1988.
- [5] Processing Science of Advanced Ceramics, I.A. Aksay, G.L. McVay, D.R. Ulrich (Eds.), MRS Symp. Proc., vol. 155, 1989.
- [6] Better Ceramics Through Chemistry IV, B.J.J. Zelinski, C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), MRS Symp. Proc., vol. 180, 1990.
- [7] Eurogel '91 Proceedings, S. Vilminot, R. Nass, H. Schmidt (Eds.), Elsevier, 1992.
- [8] Better Ceramics Through Chemistry V, M.J. Hampden-Smith, W.G. Klemperer, C.J. Brinker (Eds.), MRS Symp. Proc., vol. 271, 1992.
- [9] Better Ceramics Through Chemistry VI, A.K. Cheetham, C.J. Brinker, M.L. Mecartney, C. Sanchez (Eds.), MRS Symp. Proc., vol. 346, 1994.
- [10] C.J. Brinker, G.W. Scherer, Sol–Gel Science, The Physics and Chemistry of Sol–Gel Processing, Academic Press, New York, 1990.
- [11] D.D. Dunuwila, C.D. Gagliardi, K.A. Berglund, Chem. Mater. 6 (1994) 1556–1562.
- [12] C. Sanchez, F. Babonneau, S. Doeuff, A. Leautic, in: J.D. Mackenzie, D.R. Ulrich (Eds.), Ultrastructure Processing of Advanced Ceramics, Wiley, New York, 1988, pp. 77–87.
- [13] A. Leautic, F. Babonneau, J. Livage, Chem. Mater. 1 (1989) 240–247.
- [14] C.D. Gagliardi, D. Dunuwila, K.A. Berglund, in: B.J.J. Zelinski, C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), Better Ceramics Through Chemistry IV, MRS Symp. Proc., vol. 180, 1990, pp. 801–805.
- [15] C. Sanchez, P. Toledano, F. Ribot, in: B.J.J. Zelinski, C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), Better Ceramics Through Chemistry IV, MRS Symp. Proc., 180, 1990, pp. 47–59.
- [16] N.J. Phillips, S.J. Milne, N.J. Ali, J.D. Kennedy, J. Mater. Sci. Lett. 13 (1994) 1335–1537.
- [17] S. Barboux-Doeuff, C. Sanchez, Mater. Res. Bull. 29 (1994) 1–13.
- [18] C.D. Chandler, C. Roger, M.J. Hampden-Smith, Chem. Rev. 93 (1993) 1205–1241.
- [19] C. Sanchez, J. Livage, M. Henry, F. Babonneau, J. Non-Cryst. Solids 100 (1988) 65–76.
- [20] P.P. Phule, F. Khairulla, in: B.J.J. Zelinski, C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), Better Ceramics Through Chemistry IV, MRS Symp. Proc., vol. 180, 1990, pp. 527–532.
- [21] S. Doeuff, M. Henry, C. Sanchez, J. Livage, J. Non-Cryst. Solids 89 (1987) 206–216.
- [22] I. Laaziz, A. Larbot, A. Julbe, C. Guizard, L. Cot, J. Sol. State Chem. 98 (1992) 393–403.
- [23] H.N. Al-Shareef, K.R. Bellur, O. Auciello, X. Chen, A.I. Kingon, Thin Solid Films 252 (1994) 38–43.
- [24] M.J. Munoz-Aguado, M. Gregorkiewitz, A. Larbot, Mater. Res. Bull. 27 (1992) 87–97.
- [25] R.A. Assink, R.W. Schwartz, Chem. Mater. 5 (1993) 511–517.
- [26] K.C. Pande, R.C. Mehrotra, Z.f. anorg. u. allg. Chemie 290 (1957) 95–100.
- [27] D.C. Bradley, R.C. Mehrotra, D.P. Gaur, Metal Alkoxides, Academic Press, New York, 1978.
- [28] D.G. Niyogi, S. Singh, A. Saini, R.D. Verma, J. Fluorine Chem. 66 (1994) 153–158.
- [29] R. Ahlfänger, H. Bertagnolli, T. Ertel, B. Friedrich, A. Helmerich, U. Kolb, R. Naß, D. Peter, H. Schmidt, in: S. Vilminot, R. Nass, H. Schmidt (Eds.), EUROGEL '91, Elsevier, 1992, pp. 275–282.
- [30] S. Doeuff, Y. Dromzee, F. Taulelle, C. Sanchez, Inorg. Chem. 28 (1989) 4439–4445.
- [31] A. Leautic, R.E. Riman, J. Non-Cryst. Solids 135 (1991) 259–264.
- [32] T.M. Alam, T.J. Boyle, C.D. Buchheit, R.W. Schwartz, J.W. Ziller, in: A.K. Cheetham, C.J. Brinker, M.L. Mecartney, C. Sanchez (Eds.), Better Ceramics Through Chemistry VI, MRS Symp. Proc., vol. 346, 1994, pp. 35–40.
- [33] S. Doeuff, Y. Dromzee, C. Sanchez, C.R. Acad. Sci. Paris, 308 Serie II (1989) 1409–1412.
- [34] I. Laaziz, A. Larbot, C. Guizard, J. Durand, L. Cot, J. Joffre, Acta Cryst. C46 (1990) 2332–2334.
- [35] I. Gautier-Luneau, A. Mosset, J. Galy, Z.f. Kristal. 180 (1987) 83–95.
- [36] U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich, C. Chau, Chem. Mater. 4 (1992) 291–295.
- [37] C.E. Holloway, J. Chem. Soc., Dalton Trans. (1976) 1050–1054.
- [38] F. Babonneau, S. Doeuff, A. Leautic, C. Sanchez, C. Cartier, M. Verdagner, Inorg. Chem. 27 (1988) 3166–3172.