

Preparation of Forsterite by Pyrolysis of a Xerogel: The Effect of Water

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The structural evolution of forsterite (Mg_2SiO_4) during pyrolysis of a xerogel in a controlled atmosphere was studied by magic-angle sample spinning ^{29}Si NMR and FTIR spectroscopy and by thermal analysis. The changes above 600 °C depended strikingly on the water content of the atmosphere used for calcination; when water was added, the xerogel converted cleanly to forsterite, beginning below 600 °C. The smooth structural evolution from predominantly linear $-\text{O}-\text{Si}-\text{O}-\text{Si}-$ chains to isolated silicon centers reflects the high degree of homogeneity of the xerogel. Heterocondensation reactions are proposed to account for the gradual linking of these centers by $\text{O}-\text{Mg}-\text{O}$ units (formed from slowly hydrolyzed $-\text{OMgOMe}$ groups). On heating the xerogel at 800 °C in the absence of added water, an unidentified phase developed, which converted to forsterite above 800 °C.

Introduction

Forsterite (Mg_2SiO_4) is the magnesium-rich end member of olivine, $(\text{Fe,Mg})_2\text{SiO}_4$, which is a major component of the upper mantle of the Earth and is thought to be a principal component of interstellar dust particles. Extensive studies on the physical properties and high-pressure polymorphs of forsterite have been carried out mainly to understand geological phenomena such as earthquakes.¹ Polycrystalline forsterite has been synthesized by conventional solid state reaction of MgO and SiO_2 ,^{2,3} coprecipitation,⁴ organic polymerization,⁵ and various sol-gel methods,^{6,7} which include a H_2O_2 -assisted process.⁸ Intermediates that formed during the H_2O_2 -assisted sol-gel synthesis have been characterized by GLC analysis of the head space,⁹ and by ^{29}Si and ^{25}Mg NMR spectroscopy.¹⁰ The crystallization of the xerogel has also been studied by in situ high-temperature XRD and thermal analysis, which revealed the formation of an unidentified crystalline phase around 800 °C from xerogels that contained more than ~1% carbon.¹¹

The synthesis methodology has been further extended to enstatite¹² and chromium-doped forsterite,¹³ an opti-

cal material that tunably lases near the technologically attractive wavelength of 1.2 μm . Polycrystalline chromium-doped forsterite, prepared by the H_2O_2 -assisted sol-gel method, has been used as feedstock for single-crystal growth by the floating zone method in an oxygen atmosphere.¹³

The reaction mechanisms of various sol-gel routes to SiO_2 have been extensively studied and recently reviewed;¹⁴ most studies have focused on the sol stage. Structural change (shrinkage) during heating has been examined and related to condensation reactions occurring in the solid state.¹⁵ Little work of this type has been done on the SiO_2 - MgO system; solid-state NMR studies have focused on silicate and aluminate systems.^{16,17} Solid-state ^{29}Si magic-angle sample spinning (MASS) NMR was used to study the pyrolysis characteristics of coprecipitated precursors to forsterite.¹⁸ Several ^{29}Si MASS NMR studies were also carried out on single crystals of forsterite,^{19,20} but none has been done on a xerogel precursor to forsterite.

In this study, the structural evolution of silicon centers was examined by solid-state ^{29}Si MASS NMR spectroscopy during the interrupted pyrolysis of a

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xerogel synthesized via the H_2O_2 -assisted sol-gel method.⁸ In conjunction with thermal analysis and FTIR spectroscopy, the striking influence of water on the formation of intermediates has been examined. Some novel heterocondensation reactions are proposed.

Experimental Section

General Techniques. Magnesium pellets (99.95+%) and tetraethylorthosilicate (TEOS), 99+%, were used as received from Aldrich Chemical Co. All other materials were reagent grade. Synthesis procedures that involved solutions were performed under a dry and oxygen-free argon atmosphere.²¹

Powder X-ray diffraction patterns were obtained with a Scintag Model PADX diffractometer. Simultaneous TGA and DTA were carried out on a Seiko Model TG/DTA-320 instrument. A Mattson FTIR GL-4020 spectrometer was used to take IR spectra of powders in 1 cm diameter KBr pellets, which were pressed in an evacuable die (Perkin-Elmer Model 186-0025) under vacuum.

Solid-state NMR spectra were taken on a Bruker CXP 200 NMR spectrometer with a 4.7 T magnet using a 7 mm diameter double-resonance MASS probe purchased from Doty Scientific Inc. (Columbia, SC). The resonance frequency for ^{29}Si was 39.757 MHz. ^{29}Si NMR spectra are referenced to $(\text{CH}_3)_4\text{Si}$ using tetrakis(trimethylsilyl)silane as an external standard. Proton decoupling was used for all experiments. Spectra were acquired using a Bloch decay sequence (90° acquire). Pulses (90°) were 5 μs in duration, and recycle delays ranged from 1 to 30 s. A magic-angle spinning rate of 4 kHz was typical. Spectra were processed with FELIX (Biosym Technologies, San Diego, CA) on a DEC Station 5000/200. Despite signal averaging each spectrum for 8–12 h, spectra for heat treatments to 600 °C have low signal-to-noise ratios because features are quite weak and broad. When multiplied to have the same peak height as that from a well-crystallized sample, these spectra are noisy but show the trends in chemical shift behavior.

“Dry” gas refers to gas generated by passing compressed gas through a column of Mallinckrodt Aquasorb, and “humidified” gas corresponds to that prepared by passing the compressed gas through water (~50 mL/min) via a fine-fritted tube in a 1 L gas washing bottle. The xerogel was held in fused silica containers when heated in a tube furnace (Lindberg Model 54032A).

Sample Preparation. The precursor to forsterite, a xerogel, was synthesized by the H_2O_2 -assisted sol-gel method.⁸ To determine the effect of water on pyrolysis behavior, the xerogel was heated successively to 200, 400, 600, 800, and 1000 °C, in dry or humidified air at a ramp rate of 100 °C/h. Each sample was held at the final temperature for 5 min, allowed to cool to room temperature, and then examined by several analytical techniques.

Results and Discussion

The procedures used for the preparation of the xerogel by the H_2O_2 -assisted sol-gel method are shown schematically in Figure 1.⁸ Unlike other sol-gel methods, no catalyst is added. The use of H_2O_2 as the hydrolyzing reagent suppresses the formation of precipitates, possibly through the formation of a magnesium hydroperoxide intermediate.^{10,13} To minimize supersaturation, the reagents for hydrolysis (30% H_2O_2 and H_2O) were diluted with methanol prior to addition and were added very slowly while the reaction mixture was stirred vigorously.

Spectroscopic and Thermal Analysis. Prompted by differences observed by in situ XRD analysis during

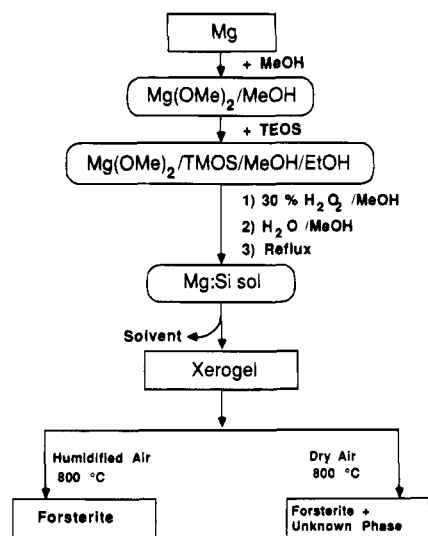


Figure 1. Schematic outline of the synthesis of forsterite xerogel by the H_2O_2 -assisted sol-gel method.⁸

pyrolysis and crystallization of the forsterite xerogel depending on the humidity of the atmosphere,¹¹ we studied the pyrolysis of the xerogel using NMR. Figures 2 and 3 show the ^{29}Si MASS NMR spectra of xerogels after heat treatment in either dry or humidified air, respectively. The NMR spectrum of the xerogel, as prepared, showed a broad peak centered around -82 ppm, which corresponds to mainly Q^2 coordinated silicon.²² The notation Q^n designates the number of siloxane ligands around silicon, $(\equiv\text{SiO})_n\text{Si}(\text{OR})_{4-n}$.^{25,26} The relationship between Q value and the chemical shift for a few magnesium-containing silicates is shown in Figure 4. Superimposed on the plot is a spectrum of the unheated precursor xerogel. There are only a few data points from the literature,^{23–26} yet the trend is consistent with the general relationship between chemical shift and known silicate structures. Although the trend suggests a predominantly Q^2 structure, minor amounts of other coordinations (Q^1 and Q^3) are probably present, considering the width of the peak.

No significant changes were observed in the spectra due the moisture content until the temperature reached ~200 °C. In the NMR spectra of xerogels heated in dry air at 400 °C, the broad peak shifted upfield to -72 ppm. The peak from the xerogel heated in humidified air was narrower and more symmetrical than that from the counterpart heated in dry air. This upfield shift of about 10 ppm is interpreted as a change in the silicon site from primarily Q^2 to primarily Q^1 and suggests the breaking of Si-O-Si linkages and the formation of -Si-O-Mg- units, which are described in more detail below.

The ^{29}Si NMR spectrum of the xerogel that was heated in dry air at 600 °C still showed a broad peak centered at -70 ppm, whereas that of the sample heated at 600 °C in humidified air contained a much less intense, broad peak centered around -70 ppm and a

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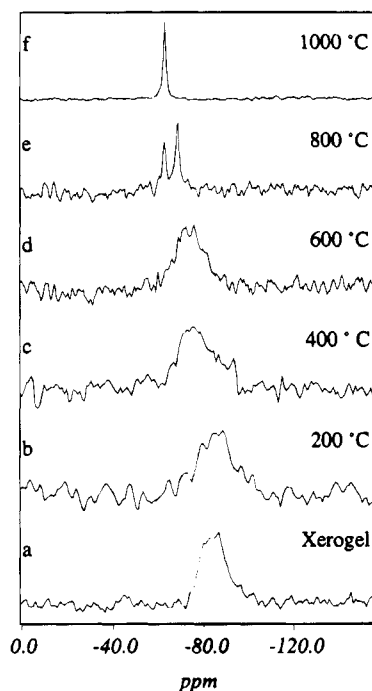


Figure 2. Solid-state ^{29}Si MASS NMR spectra taken from a forsterite xerogel heated in dry air, at a ramp of 100 °C/h. The xerogel was heated to the following temperatures at 100 °C/h and held there for 5 min: (b) 200, (c) 400, (d) 600, (e) 800, and (f) 1000 °C. The spectrum of the xerogel, as prepared, is shown in (a).

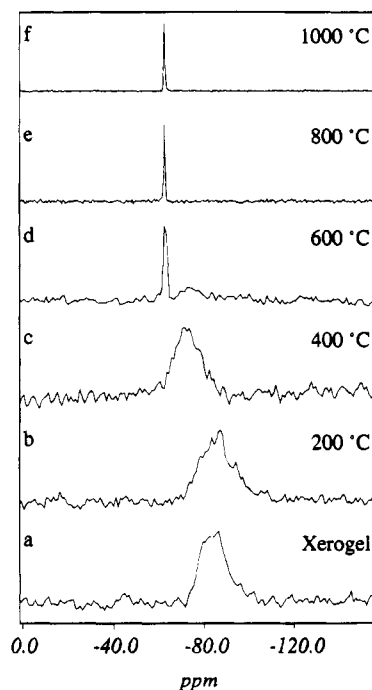


Figure 3. Solid-state ^{29}Si MASS NMR spectra taken from the forsterite xerogel heated in humidified air. The xerogel was heated to the following temperatures at 100 °C/h and held there for 5 min: (b) 200, (c) 400, (d) 600, (e) 800, and (f) 1000 °C. The spectrum of the xerogel, as prepared, is shown in (a).

narrow peak centered at -62 ppm, which we assign to forsterite. The ^{29}Si NMR chemical shift of forsterite has been reported at -61.9 ppm.²⁵ In the spectrum of the xerogel heated at 800 °C in humidified air, the broad peak disappeared, and the peak at -62 ppm became very narrow, typical of well-crystallized forsterite. When

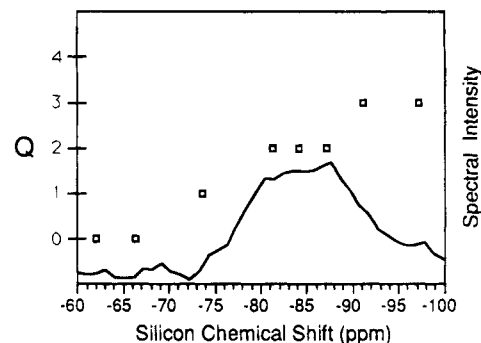


Figure 4. The relationship of silicon environment (Q value) versus ^{29}Si NMR chemical shifts for several magnesium-containing silicates,^{23–26} (squares, left scale) The NMR spectrum of the as-prepared forsterite precursor xerogel is superimposed, (solid line, right scale) showing the predominantly Q^2 nature of the silicon sites therein.

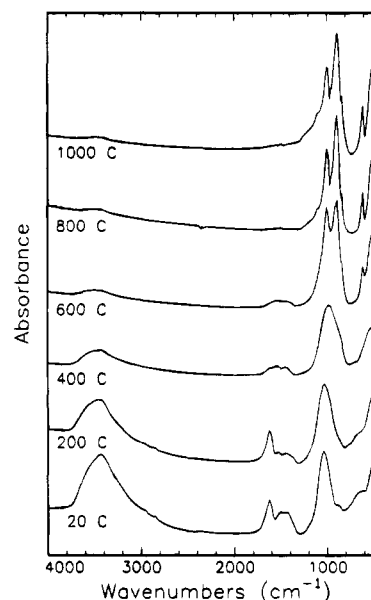


Figure 5. FTIR spectra taken from the forsterite xerogel heated in humidified air for 5 min at various temperatures. The heating rate was 100 °C/h. The spectrum of the xerogel as prepared is shown at the bottom.

the xerogel was heated at 800 °C in dry air, two sharp peaks developed at -62 and -68 ppm (Figure 2e). The former is assigned to forsterite, and the latter to an unidentified intermediate phase, which is currently under investigation. Only a single sharp resonance at -62 ppm (from forsterite) was present in spectra of xerogels heated to 1000 °C (see Figures 2f and 3f) whether the atmosphere was dry or humidified.

FTIR spectra taken in conjunction with the NMR studies are shown in Figures 5 and 6. The IR spectra for the xerogels as prepared and those heated at 200 °C are quite similar, regardless of the humidity during heating. Broad peaks, interpreted as arising from O-H groups in various environments (M-OH, H_2O , ROH, etc.), are apparent around 3400 and 1640 cm^{-1} .²⁷ The C-H stretching modes of alkoxy groups appear as weak peaks at 2850 and 2950 cm^{-1} . The peaks around 1000 cm^{-1} are assigned to Si-O stretching modes, and the ones around 500 cm^{-1} to Mg-O stretching or Si-O

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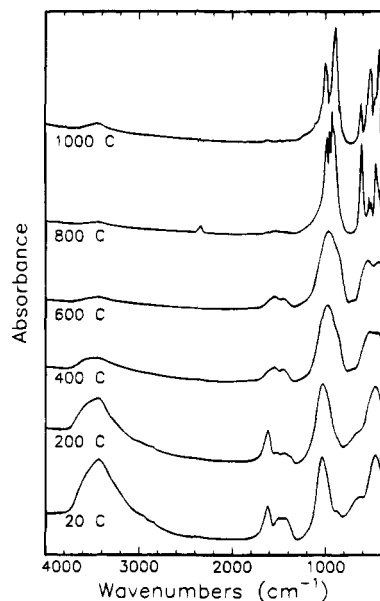


Figure 6. FTIR spectra taken from the forsterite xerogel heated in dry air for 5 min at various temperatures. The heating rate was 100 °C/h. The spectrum of the xerogel as prepared is shown at the bottom.

bending modes.²⁸ Both spectra of the xerogel heated at 400 °C (see Figures 5 and 6) show the peaks from $\nu(\text{O}-\text{H})$ diminished, and peaks from $\nu(\text{C}-\text{H})$ are absent. The IR spectrum for the xerogel heated at 600 °C in humidified air (Figure 5) shows several sharp peaks that correspond to those of forsterite as well as some broad peaks.²⁹⁻³¹ Only the broad peaks are observed in the spectrum of the xerogel heated in dry air (Figure 6). XRD analysis of the xerogel heated in humidified air showed that it was partially crystalline (peaks from forsterite were evident) whereas the xerogel heated in dry air was amorphous, which is consistent with the NMR spectra (see above).

The FTIR spectra of xerogels heated at 800 °C show strikingly different features depending on whether the air was humidified or dry. The IR spectrum of the xerogel heated at 800 °C in humidified air (Figure 5) had peaks at 1001, 961.5, 900.5, 842, 616.5, 522.5, 509 (sh) 482 (sh), 466.5, and 436 cm^{-1} and was the typical spectrum of crystalline forsterite.^{30,31} The spectrum of the sample heated at 800 °C in dry air (Figure 6) had peaks at 2349, 1547, 1543, 1509, 1474, 1566, 1449, 982, 951, 922, 609, 536, 513, and 472 cm^{-1} . The peak at 2349 cm^{-1} is assigned to carbon dioxide trapped within the xerogel. The 11 cm^{-1} difference from the value of the asymmetric stretching frequency reported for gaseous CO_2 (2360 cm^{-1})³² may be caused by partial adsorption on the interior walls of closed pores. Peaks around 1500 cm^{-1} are assigned to unidentate carbonates.³³ Other peaks around 500 cm^{-1} are probably due to $\text{Mg}-\text{O}$ stretching or $\text{Si}-\text{O}$ bending modes.²⁹ Spectra for the xerogel heated at 1000 °C show only peaks for crystal-

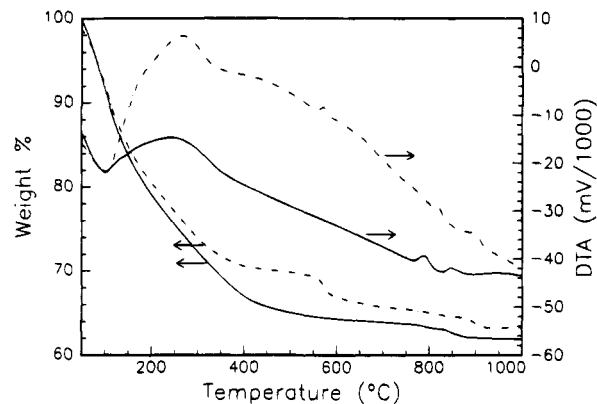


Figure 7. TGA and DTA traces of the forsterite xerogel heated in humidified air (—), or in dry air (---). The heating rate was 10 °C/min.

line forsterite, regardless of whether the air was dry or humidified.

Simultaneous TGA and DTA curves obtained during heating of the xerogel are shown in Figure 7. The large weight loss ($\sim 20\%$) below 200 °C accompanies a broad endotherm (centered at ~ 101 °C) which indicates the loss of adsorbed solvent.³⁴ A broad exotherm centered around 250 °C coincides with another weight loss of 10–15%. Between 200 and 450 °C, less weight ($\sim 5\%$) is lost in dry air than in humidified air. In dry air, the cause of a $\sim 3\%$ weight loss during a minor exotherm at ~ 570 °C is unknown. At higher temperatures, two exotherms are observed at 789 and 845 °C in humidified air and at 823 and 900 °C in dry air. These events occur ~ 50 °C lower in humidified air than in dry air. Water vapor may promote loss of most of the residual organic groups below 400 °C, leaving little carbonaceous residue to retard crystallization of forsterite.¹¹ The appearance of two consecutive exotherms around the crystallization temperature has been observed in several transition-metal-doped forsterite xerogels.^{11,35} In most cases, $\sim 1-2\%$ weight loss accompanied the second exotherm. The cause of these doubled exotherms during crystallization is not known. Since they have not been observed in enstatite,¹² magnesium oxide,³⁶ or fluorotalc³⁷ xerogels that were synthesized by similar H_2O_2 -assisted sol-gel methods, the structural development of the xerogel into forsterite may proceed via an intermediate that has sufficient stability to render an exotherm.

Reaction Pathways. From the ^{29}Si NMR spectra (see above), the xerogel as prepared consists mostly of Q^2 species, with the possibility of minor components of Q^1 and Q^3 species. This predominantly linear structure does not change below 200 °C, suggesting that under these mild conditions, no reaction occurs at the silicon centers. In this temperature regime, a $\sim 20\%$ weight loss occurs, accompanied by a broad endotherm (Figure 7). This thermal event is typical of the loss of adsorbed solvents. An endotherm near 100 °C, observed during pyrolysis of a silica xerogel, was interpreted as desorption of solvent.³⁴ The IR spectrum of the xerogel, after it was heated to 200 °C, shows the $\nu(\text{O}-\text{H})$ and $\nu(\text{C}-\text{H})$

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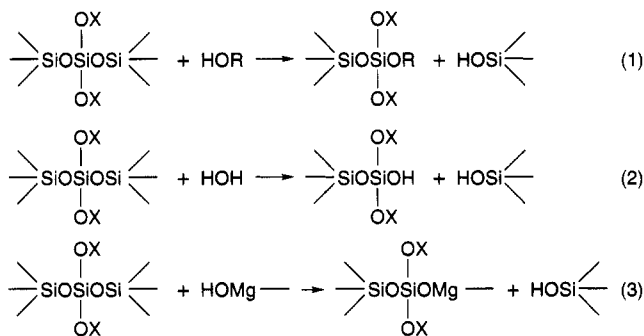
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peaks unchanged, even after loss of solvent. Therefore, these vibrational peaks correspond to bound groups. This conclusion is supported by the loss of the strong odor of methanol from the xerogel after it was heated at 200 °C. From these observations, it is clear that little reaction occurs under 200 °C, other than the loss of adsorbed species.

Above 200 °C, the ^{29}Si NMR peak shifts downfield. The change in chemical shift is interpreted as a change in the silicon sites from primarily Q^2 to primarily Q^1 sites. This structural change coincides with a weight loss of 10–15%, accompanied by a broad exotherm centered around 230 °C. An exothermic condensation reaction around 275 °C during pyrolysis of a borosilicate xerogel has been reported.³⁸ The transition from Q^2 to Q^1 involves breaking a $-\text{Si}-\text{O}-\text{Si}-$ bond. The breaking of one such bond can lead to three different structures, which are shown as reaction products in eqs 1–3. Here



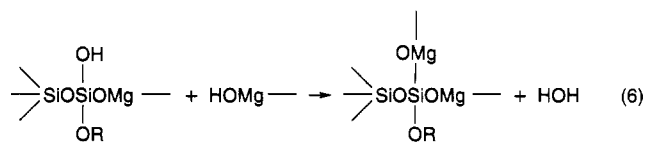
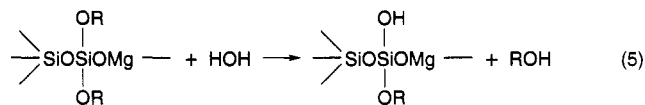
$-\text{OX}$ depicts any of the functional groups $-\text{OMgO}-$, $-\text{OH}$, or $-\text{OR}$. The symbol $-\text{OR}$ can represent either methoxy or ethoxy. Ethoxy ligands on TEOS exchange readily with methoxy ligands from the solvent, methanol, catalyzed by magnesium methoxide.^{10,39} Because excess methanol is used, almost all organic ligands around silicon centers are expected to be methoxides, after the solvent is removed. Therefore, $-\text{OR}$ in the structure essentially represents $-\text{OMe}$. The exchange reaction (eq 3) is preceded by hydrolysis (eq 4).



The second methoxide group of $\text{Mg}(\text{OMe})_2$ is known to hydrolyze *much* more slowly than the first; the known compound, MeOMgOH is unreactive toward a moderate (3–5-fold) excess of water.^{40,41} In comparison with an all-silicon system, the presence of the magnesium component alters the chemistry of the intermediates substantially.

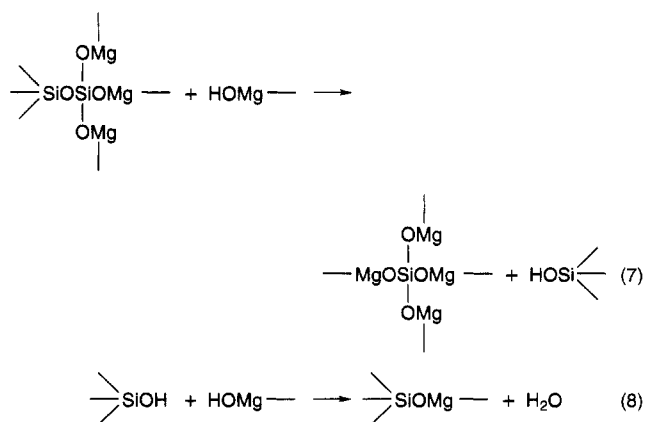
All three reactions (eqs 1–3) are expected to occur during the heating between 200 and 400 °C. A likely process is a nucleophilic attack at silicon by the somewhat basic HOMg--- group (eq 3). Because condensation and densification are favored thermodynamically in this temperature region,⁴² products of the first two reactions (eqs 1 and 2) could react with HOMg--- groups to eventually give the same product as that shown in eq 3. The replacement of $-\text{OMe}$ by $-\text{OH}$ (eq 4) cannot

account for all the weight lost. Therefore, additional reactions must be involved. Two plausible concurrent reactions are shown in eqs 5 and 6. Since 1 equiv of



water is involved in the hydrolysis of ROMg--- (eq 4), which precedes the heterocondensation (eq 6), the net weight loss is comparable to the loss of one MeOH and replacement of two $-\text{OMe}$ by two $-\text{OH}$; 1 equiv of water will be consumed for each $-\text{Si}-\text{O}-\text{Mg}-$ unit formed. Therefore, a larger weight loss is expected and observed (~5%, by TGA) when the xerogel is heated in a humidified atmosphere. These reactions decrease the weight by releasing bound methoxy and hydroxy ligands and increase the fraction of metal oxide network by forming $-\text{Si}-\text{O}-\text{Mg}-$ units by heterocondensation. It is interesting to note that the major weight loss observed by TGA and the $\text{Q}^2 \rightarrow \text{Q}^1$ change observed by NMR may originate from two different types of reaction, viz., eqs 5 and 6, or eqs 1–3, respectively.

The xerogel heated at 600 °C has a fairly well-formed forsterite structure when high humidity is present in the atmosphere, whereas when a dry atmosphere is used, the Si sites are still primarily Q^1 with lesser amounts of Q^0 and Q^2 . The ^{29}Si NMR line shape for the xerogel heated at 600 °C in dry air is broad, signifying a variety of local environments for silicon. The powder XRD pattern of the xerogel heated at 600 °C in humidified air shows the sample is a mixture of crystalline forsterite and amorphous material, whereas the xerogel heated in dry air at the same temperature is completely amorphous. Therefore, it seems clear that the cleavage of the $\text{Si}-\text{O}-\text{Si}$ link (eq 7), followed by condensation of the resulting silanol (eq 8), occurs much earlier when water is provided externally.



As the xerogel is heated at 200–400 °C, the alkoxy ligands are gradually eliminated via the hydrolysis and condensation reactions described previously. Alkoxy ligands are not present around 500 °C when the xerogel is heated in humidified or dry air as judged by the absence of peaks for C–H stretching vibrations in the

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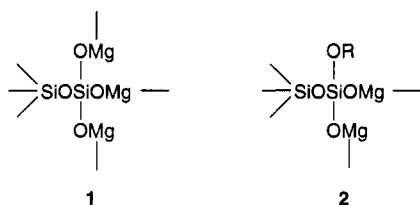
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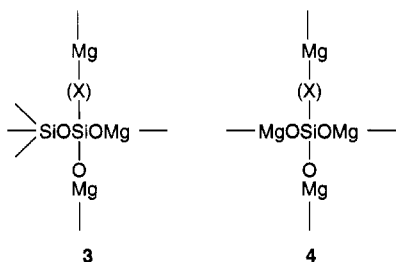
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IR spectra (Figures 5 and 6). Previous work showed that after being calcined at 600 °C in dry air the carbon content of a forsterite xerogel was over 2% by weight.¹¹ When calcination was carried out in humidified air at 600 °C, the carbon content was less than 1%. The present results indicate that most of the carbon in the calcined xerogels is in an inorganic form above 400 °C. As noted earlier, the two broad bands at 1553 and 1460 cm^{-1} in the IR spectrum of the xerogel heated to 600 °C in dry air suggest the presence of carbonate. Subsequent thermal decomposition of this carbonate between 600 and 800 °C probably causes the peak at 2349 cm^{-1} , which is tentatively assigned to trapped CO_2 . The relative intensity of the carbonate IR peaks is lower when humidified air is used.

Plausible local structures in the samples heated in dry or humidified air around 500 °C are 1 and 2.



Structure 1 is suggested as a dominant local structure for the xerogel heated in humidified air. This species readily transforms into forsterite (Q^0), possibly via eq 7, starting around 560 °C, the onset temperature for crystallization assessed by in situ, high-temperature XRD (HTXRD).¹¹ When the xerogel is heated in a dry atmosphere, more carbon-containing components remain, as noted above probably because hydrolysis (eq 5) and heterocondensation (eq 6) are not complete in the lower temperature range (200–400 °C), chiefly because of a deficiency of water (one extra molecule of water is needed for formation of each $-\text{SiOMg}-$ fragment). The structure of the Q^1 species at 600 °C may resemble 3 in which X is a carbon-containing group, possibly a carbonate.



When the xerogel is heated at 800 °C under anhydrous conditions, two silicon environments are observed in the ^{29}Si NMR spectrum; one of these coincides with that of forsterite. Under these conditions, two crystalline phases were observed in the previous HTXRD study, one of which was forsterite.¹¹ The ^{29}Si NMR chemical shift at -68 ppm is at the upfield end of the range for Q^1 species and at the downfield end of the range for Q^0 species.^{25,26} Since the chemical shift at 600 °C is still at -70 ppm, the remaining carbon-containing groups may decompose into carbon or CO_2 , while some $-\text{SiOSi}-$ fragments are extant. If these fragments react further, local structure 4 is proposed; otherwise structure 3 obtains. If X were oxygen in 4, the structure

at silicon might be similar to that proposed to account for a peak (at -68 ppm) assigned to one of the three Si^{IV} sites in the garnet, $\text{Mg}_4\text{Si}^{\text{VI}}\text{Si}^{\text{IV}}_3\text{O}_{12}$, which was synthesized at high pressure.⁴³ X may also represent a carbon-containing component, possibly CO_n .¹¹ The identity of this intermediate is under investigation.

An important outcome of the present study concerns the issue of the homogeneity of the xerogel. A high degree of homogeneity of the products synthesized by the H_2O_2 -assisted sol-gel method was suggested in previous reports on the basis of empirical observations, e.g., absence of precipitates, transparency of the sol and xerogel, etc.^{8–10,37} Moreover, forsterite began to crystallize at the remarkably low temperature of 560 °C for a pulverized xerogel powder,¹¹ and enstatite (MgSiO_3), a common byproduct of inhomogeneity, was never observed. In contrast, the formation of enstatite (Q^2) was observed by solid-state ^{29}Si MASS NMR during the crystallization of a coprecipitated precursor to forsterite, which developed NMR peaks for both Q^0 and Q^2 upon heating.¹⁸ The present NMR results reflect the homogeneity of the product when the xerogel is calcined in a humidified atmosphere. The gradual transition from primarily Q^2 to mostly Q^1 and finally to Q^0 , without development of Q^3 or Q^4 sites, is strong evidence that the silicon environment in the xerogel is homogeneous; the “environment” is the distance sensed by the NMR method, viz., several angstroms. If the xerogel were inhomogeneous, Q^3 or Q^4 species would be detected as the result of condensation reactions that formed polymorphs of SiO_2 .

Conclusions

Hydrolysis and condensation reactions occurring during pyrolysis of a xerogel precursor to forsterite have been deduced from structural changes observed by solid-state ^{29}Si MASS NMR and FTIR spectroscopy and by thermal analysis. The changes above 600 °C depended strongly on whether or not water was present in the atmosphere. The need for additional water during calcination may be a consequence of (1) the relatively modest amount of water (and H_2O_2) used for the hydrolysis of the starting alkoxides (sufficient protons were available to react with $\sim 90\%$ of the alkoxide groups present, ignoring any water formed from condensation) and (2) of the low reactivity of residual $-\text{OMgOMe}$ groups.^{40,41} When the atmosphere for calcination was humidified, the xerogel converted cleanly to forsterite. The structural development around silicon centers reflects the high degree of homogeneity of the xerogel, and the gradual linking of these centers by $-\text{OMgO}-$ units. The H_2O_2 -assisted sol-gel method may be very useful in preparing nanocomposite materials, for which a high degree of homogeneity is essential.

When the atmosphere for pyrolysis was dried, a mixture of two crystalline phases developed. This may be caused by residual carbon generated by decomposition of residual organic ligands.

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