

Crystallization of Forsterite Xerogel under Carbon Dioxide: A New Crystalline Material Synthesized by Homogeneous Distribution of Carbonaceous Component into Forsterite Xerogel

Me Young Song, Sue Joo Kim, Hye Young Kwon, Seon Hui Park, Dong Gon Park,*
Ho-Jin Kweon,[†] Young-Uk Kwon,[†] and James M. Burlitch[‡]

Department of Chemistry, Sookmyung Women's University, Seoul 140-742, Korea

[†]Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea

[‡]Department of Chemistry, Cornell University, Ithaca, NY 14850, USA

Received September 7, 1998

By heating the magnesiumsilicate (Mg_2SiO_4 : forsterite) xerogel in carbon dioxide, carbonaceous component was intentionally introduced into the amorphous solid precursor. Carbon was introduced homogeneously as unidentate carbonate. Upon being heated at 800 °C in carbon dioxide, the xerogel which had homogeneously distributed carbonaceous component in it crystallized into a single phase product of a new crystalline material, which had approximate composition of $\text{Mg}_8\text{Si}_4\text{O}_{18}\text{C}$. The powder X-ray diffraction pattern of the new crystalline material did not match with any known crystalline compound registered in the powder diffraction file. Crystallization from amorphous xerogel to the new crystalline phase occurred in a very narrow range of temperature, from 750 °C to 850 °C in carbon dioxide, or in dry oxygen. Upon being heated above 850 °C, carbonaceous component was expelled from the product, accompanied by irreversible transition from the new crystalline material to forsterite.

Introduction

Sol-gel method is very versatile synthetic process to prepare solid products, especially various mixed metal oxides.¹ Two major advantageous aspects can be pointed out for the method, when it is compared to the conventional solid state reaction. Compared to the conventional solid state reaction,² sol-gel method provides more means to control the morphology of the final solid products. The products can be fabricated into various different shapes, such as particles,³ thin films,⁴ monoliths,⁵ composites,⁶ or even fibers.⁷ Also, very high level of compositional homogeneity can be attained through the method, because molecular reactants are used. The attainment of the homogeneous composition can be considered to be one of the most advantageous aspect of the sol-gel method, which can not be reproduced by any other conventional synthetic processes. As the compositional homogeneity is established in the xerogel, diffusion barrier is nearly eliminated. Therefore, crystallization proceeds readily into completion at much lower temperature and in much shorter period than in the conventional solid state reaction.^{7,8,9}

But, for mixed metal oxides whose more than two metallic constituents are involved, there are many practical obstacles in attaining such a high homogeneity in molecular level. Because reactants have different hydrolysis rates, one metallic constituent tends to react prior to the others do.¹⁰ This mismatch in rates of hydrolysis and condensation reaction results in compositional inhomogeneity. The H_2O_2 -assisted sol-gel method was devised to solve this mismatch in the reaction rates specifically between magnesium alkoxides and silicon alkoxides.⁷ In preparing magnesiumsilicates, the

H_2O_2 -assisted sol-gel method can provide very homogeneous distribution of the compositional constituents, by making the hydrolysis rates of the magnesium and silicon alkoxides become similar. By using this particular synthetic approach, various foreign constituents could be intentionally distributed homogeneously into magnesiumsilicates, especially into forsterite (Mg_2SiO_4).¹¹ Chromium was doped into forsterite by the method, producing chromium-doped forsterite which emits tunable laser at near infrared region.¹² Vanadium was also doped into forsterite by the method.¹³

In this study, we report intentional distribution of carbonaceous component into magnesiumsilicate of forsterite composition (Mg_2SiO_4)¹¹ in highly homogeneous manner via the H_2O_2 -assisted sol-gel method. Upon heat-treatment in carbon dioxide, carbonaceous component in the xerogel gave way to a formation of a newly found crystalline phase which was never reported by others.

Experimental Section

A forsterite xerogel powder was synthesized via the H_2O_2 -assisted sol-gel route.¹² To see the effect of the environmental gas on the crystallization of the forsterite xerogel, it was heated successively at 200, 300, 400, 500, 600, 700, 750, 800, 850, 900, and 1000 °C. The xerogel powder, ~40 mg for each heat-treatment, was loaded in a fused silica container, and heated at each designated temperatures for 5 min, at a ramp of 100 °C/h. The heating was carried out in a closed fused silica tube whose one end was open to an oil bubbler, and the other end to a source of gas. Four different kinds of gases were used at a flow rate of ~100 mL/min: dry oxygen, humidified oxygen, dry carbon dioxide, and humidified car-

bon dioxide. The gas was dried by passing it through a column of Mallinckrodt Aquasorb. Humidified gas was prepared by passing it through water via a fine fritted tube in a 1L gas washing bottle.

Powder X-ray diffraction (PXRD) patterns were obtained with a Scintag PAD-X diffractometer, and a Philips X'pert diffractometer. For taking the pattern from the powder heated at 800 °C, a single-crystalline zero background quartz holder was used. To obtain accurate d-spacings, PXRD pattern was taken at a slow scan from the dark gray powder of the new crystalline product produced in carbon dioxide, which was well mixed with silicon powder standard (~10 w%, ~325 mesh, Aldrich). The diffraction peak positions observed for the new crystalline phase are 21.719, 25.131, 30.023, 35.826, 36.605, 38.829, 42.291, 44.269, 47.292, 49.223, 56.620, 58.265, 60.851, 62.363, 64.416, 64.805, 66.415, 68.885, and 74.105 ($^{\circ}2\theta$). From the d-spacings obtained from the PXRD pattern, the crystal system and the unit cell parameters were calculated by the fitting program 'Teor'.¹⁴

The IR spectra were taken by using Mattson GL-4020 spectrometer and Nicolet Impact-400 spectrometer from pellets made from a mixture of the powder sample and KBr. The IR spectrum taken from the new crystalline phase showed peaks at 2349 (s), 1574 (w), 1543 (w), 1509 (vw), 1474 (vw), 1566 (vbr), 1449 (vbr), 982 (s), 951 (s), 922 (s), 609 (s), 536 (s), 513 (s), and 472 (s) cm^{-1} .

Simultaneous thermo-gravimetric and differential thermal analysis (TG/DTA) were carried out on a Seiko TG/DTA-320 instrument. The forsterite xerogel was heated in a flow of dry carbon dioxide at a rate of 100 mL/min. The temperature was ramped at 10 °C/min. The elemental analysis was carried out on powder sample which was heated under vacuum at 600 °C for 15h to remove adsorbed molecules, and sealed in an ampule under argon.

Results and Discussion

The synthesis of a new crystalline phase from forsterite xerogel was schematically described in Figure 1. The forsterite xerogel was synthesized by the H_2O_2 -assisted sol-gel method.^{7,12} Addition of H_2O_2 , instead of acid or base catalysts,¹⁵ was presumed to generate $-\text{MgOOH}$ intermediate¹⁶ which should hamper the condensation reaction of $-\text{MgOH}$ moieties while acting as a catalyst to enhance hydrolysis of silicon alkoxide. Thereby, segregation of $\text{Mg}(\text{OH})_2$ was avoided, and very homogeneous clear alcogel was obtained. Simple way to assess compositional homogeneity of the alcogel, which contains more than two metallic constituents, is to observe its turbidity. When water was added without the addition of H_2O_2 , $\text{Mg}(\text{OH})_2$ precipitated out and the solution became very turbid. Upon standing still, white precipitates of $\text{Mg}(\text{OH})_2$ segregated down on the bottom of the container. On the contrary, when H_2O_2 was used during initial hydrolysis reaction, the alcogel looked clear. In most cases, some tint of haziness was caused by nano-sized gel network. No segregation in the alcogel was observed after standing

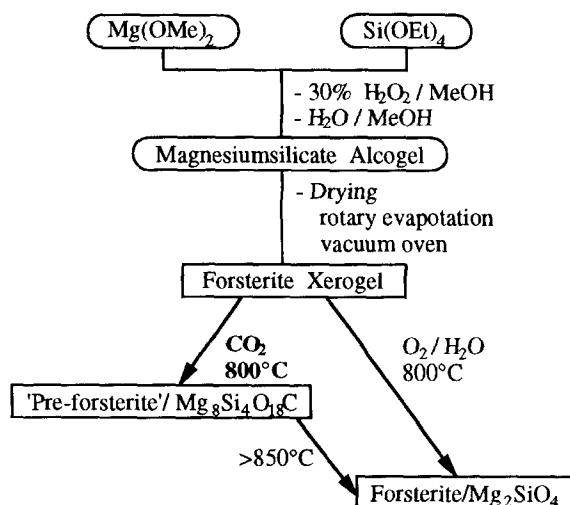


Figure 1. Schematic outline of the synthesis of a new crystalline material, which was temporarily dubbed as 'pre-forsterite', via heat treatment of forsterite xerogel in carbon dioxide gas at 800 °C. Rectangular containment represents solid state, and round one solution state.

still in closed container for up to several months.

Synthesizing the forsterite alcogel as a clear one was very important in obtaining the new crystalline phase from the forsterite xerogel, because carbonaceous component had to be distributed very homogeneously. If turbid gel was obtained by any reason, homogeneous distribution of the carbonaceous component to the xerogel apparently failed, and the new crystalline phase could not be prepared as a single phase product. One other important synthetic step to get appropriate xerogel was observed to be the way to remove alcohol from the alcogel. It was observed that the alcogel had to be dried slowly by rotary evaporation, then consecutively in vacuum oven, in order to succeed in obtaining the new crystalline phase as a single phase product. It is suggested that morphology of the forsterite xerogel, such as pore size and surface area, is also an important synthetic factor.¹⁷

It was observed that the crystallization of the forsterite xerogel proceeded through very different routes, depending on what kind of gas was used during heat treatment of the xerogel. The crystallization of the xerogel was investigated by obtaining PXRD patterns and FTIR spectra from the solid samples quenched after the heating of the xerogel reached the designated temperatures. In previous study, it was observed that the humidity of air was important synthetic variation during pyrolysis of the forsterite xerogel.¹⁸ Humidity have significant influence on the crystallization of the forsterite xerogel also in oxygen. When the xerogel was heated in humidified oxygen, the first crystalline phase developed upon being heated was forsterite, as was shown by PXRD patterns in Figure 2. Diffraction peaks for forsterite developed around 800 °C, and remained further at higher temperature. No phase other than forsterite was observed. The FTIR spectra (in Figure 3) also conformed to the PXRD observation, that the sharp peaks of Mg-O and Si-O vibra-

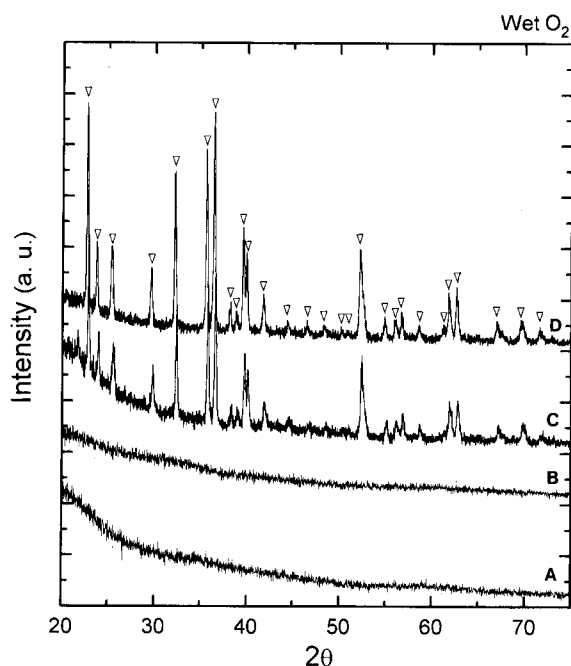


Figure 2. PXRD patterns taken from the forsterite xerogel heated in humidified oxygen. The xerogel was heated at (A) 400 °C, (B) 600 °C, (C) 800 °C, and (D) 1000 °C, for 5 minutes. Diffraction peaks for forsterite were marked by open triangles. Overall shift of the peaks was caused by using different scan range for each pattern (instrumental cause).

tional modes developed around 800 °C: at 436 and 466.5 cm^{-1} (Mg-O), and at 482(sh), 509(sh), 522.5, and 616.5 cm^{-1} (Si-O bending), and at 842, 900.5, 961.5, and 1001 cm^{-1} (Si-

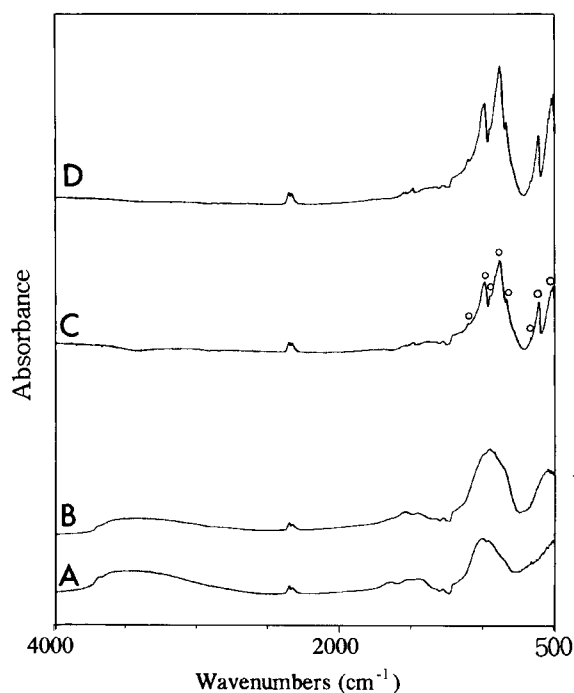


Figure 3. FTIR spectra taken from the forsterite xerogel heated in humidified oxygen. The xerogel was heated at (A) 400 °C, (B) 600 °C, (C) 800 °C, and (D) 1000 °C. The vibrational peaks designated by open circles are for crystalline forsterite.

O stretching). Those peaks coincided with the ones reported for forsterite.^{19,20}

On the contrary, the first crystalline phase developed around 800 °C was not forsterite when dry oxygen was used in heating the xerogel, as was shown by PXRD patterns in Figure 4. It was observed that the diffraction peaks of the unknown crystalline phase developed together with those of forsterite at 800 °C in dry oxygen. As the PXRD pattern from the new crystalline phase was not registered in the powder diffraction file (JCPDS),²¹ it would be described temporarily as 'pre-forsterite' for convenience in description of the new crystalline phase. The FTIR spectra also indicated the development of the 'pre-forsterite' prior to forsterite, as shown in Figure 5. When the forsterite xerogel was heated in dry oxygen, the peaks for this unknown phase appeared around 800 °C instead of forsterite. But, in both PXRD and FTIR observations, the peaks for the 'pre-forsterite' readily disappeared as the temperature was raised above 900 °C, and replaced by those for forsterite.

The powder heated at 800 °C had dark gray color, and elemental analysis showed that the powder contained ~2% carbon in it. Therefore, it was suggested that carbonaceous component should be contained in the xerogel in order to get the 'pre-forsterite'. In previous investigation by thermal analyses in air,¹⁸ it was observed that the amount of carbon residue increased as dry gas was used during pyrolysis. Because condensation reaction does not proceed into completion, some amount of alkoxy ligands remain in the xerogel.²² Apparently the source of the carbon was the residual alkoxy ligands still remained in the forsterite xerogel, when

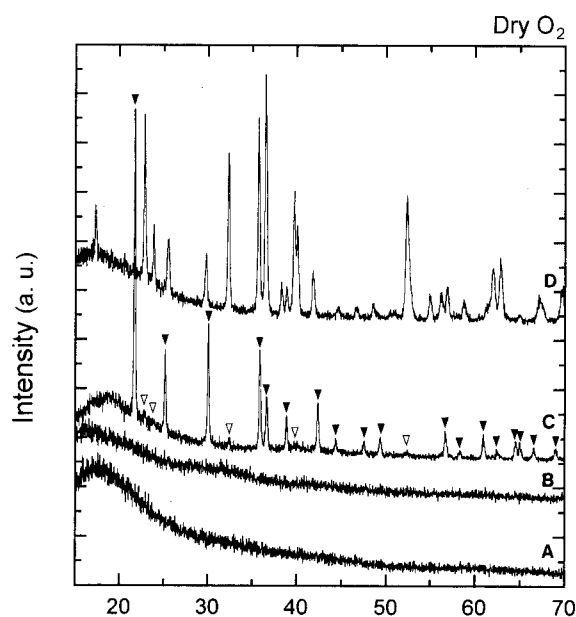


Figure 4. PXRD patterns taken from the forsterite xerogel heated in dry oxygen. The xerogel was heated at (A) 400 °C, (B) 600 °C, (C) 800 °C, and (D) 1000 °C. Diffraction peaks for forsterite were marked by open triangles. The peaks with solid triangles are for the new crystalline phase whose the pattern has not been reported by others.

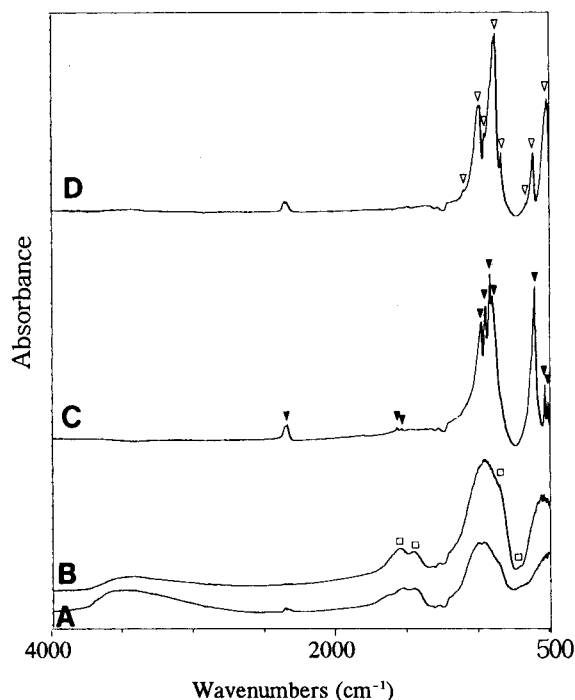


Figure 5. FTIR spectra taken from the forsterite xerogel heated in dry oxygen. The xerogel was heated at (A) 400 °C, (B) 600 °C, (C) 800 °C, and (D) 1000 °C. The vibrational peaks marked by open triangles are for forsterite, and the peaks with solid triangles are for the new crystalline phase. The peaks for carbonate were marked by open squares.

it was heated in dry oxygen. The containment of the carbonaceous component in solid samples prepared by heating the xerogel was presumed to be caused by decomposition of these alkoxy ligands. By seeing that the 'pre-forsterite' was obtained as a mixture with forsterite, the amount of the carbon provided by the organic residue was not sufficient to form the new phase exclusively. Therefore, carbon dioxide was chosen as a gas environment during heat treatment. Because major gas product upon decomposition of the residual alkoxy ligands was supposed to be carbon dioxide and carbon monoxide, the carbon dioxide environment should suppress the release of the carbonaceous component out of the solid. Thereby, the amount of the carbon provided to the solid should be increased. On the basis of this reasoning, carbon dioxide was selected as the gas environment for the heat-treatment of the forsterite xerogel.

The crystallization of the forsterite xerogel in carbon dioxide was monitored by obtaining PXRD patterns and FTIR spectra from the solid samples heated in carbon dioxide, which were shown in Figure 6 and 7. Vibrational peaks of the alkoxy groups were observed in the IR spectrum taken from the xerogel, which indicated the residual alkoxy ligands remaining in the xerogel. Those peaks were observed up to 200 °C, and replaced by broad peaks around 1500, 1000, and 600 cm^{-1} above 400 °C. As in dry oxygen, the first crystalline phase developed upon being heated was the 'pre-forsterite' rather than forsterite, in carbon dioxide. Only a phase of 'pre-forsterite' was observed at 800 °C, and

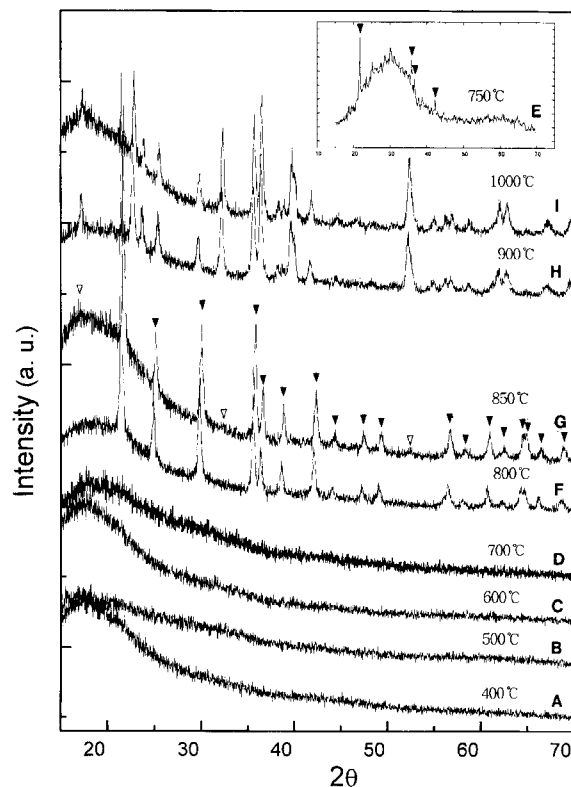


Figure 6. PXRD patterns taken from the forsterite xerogel heated in carbon dioxide. The xerogel was heated at (A) 400 °C, (B) 500 °C, (C) 600 °C, (D) 700 °C, (E) 750 °C, (F) 800 °C, (G) 850 °C, (H) 900 °C, and (I) 1000 °C. The diffraction peaks for forsterite were marked by open triangles, and for the new crystalline phase by solid ones.

no peak was observed for forsterite. Therefore, a single phase product of the 'pre-forsterite' could be synthesized by heating the forsterite xerogel at 800 °C in carbon dioxide. When further heated at 850 °C, diffraction peaks of forsterite started appearing. At 900 °C, all those peaks of 'pre-forsterite' disappeared, and replaced by those of forsterite. Therefore, there apparently is a narrow range of temperature, between 750 and 850 °C, where the 'pre-forsterite' can be obtained from the forsterite xerogel. Below the range, the crystallinity of the phase was not established, even though the local structure around Si and Mg might have appropriate settings. Above the range, it appeared that a phase transition from the 'pre-forsterite' to forsterite occurred, as was observed from the sample heated in air.¹⁸ The powder heated above 900 °C had white color, and no carbon was detected from the powder by elemental analysis. Therefore, it was presumed that the phase transition occurred because the carbonaceous component in the 'pre-forsterite' was eliminated above 900 °C. It has been reported that carbon burnout was observed around 860 °C.²³

FTIR spectrum was taken from a batch of the forsterite xerogel which was carefully heated in carbon dioxide at 600 °C, and was compared to that obtained from the xerogel heated in humidified oxygen, in Figure 8. The dark brown powder heated at 600 °C was amorphous, as was observed by PXRD. Two major differences in the IR spectrum devel-

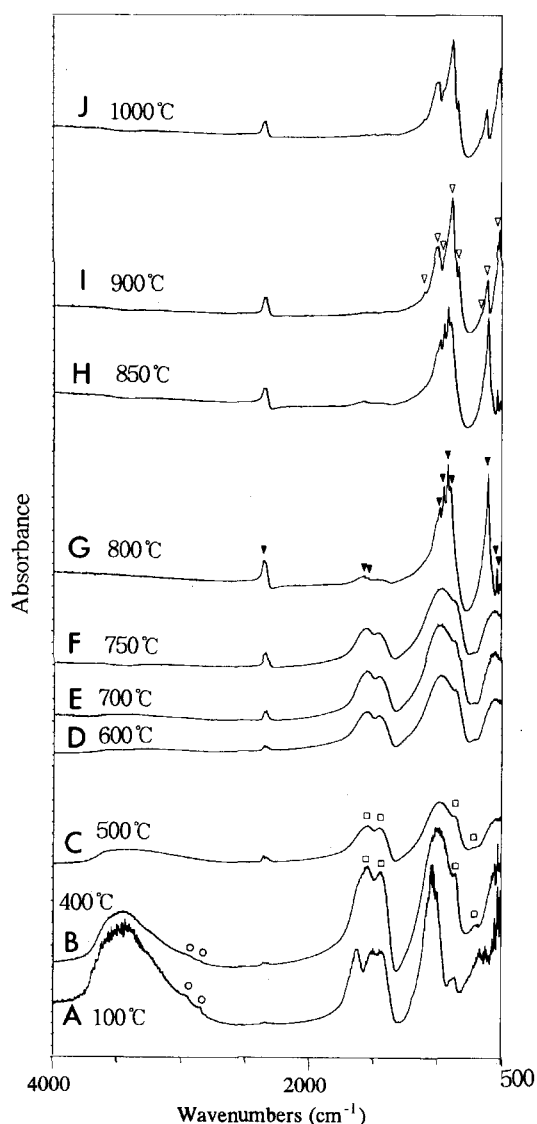


Figure 7. FTIR spectra taken from the forsterite xerogel heated in carbon dioxide. The xerogel was heated at (A) 100 °C, (B) 400 °C, (C) 500 °C, (D) 600 °C, (E) 700 °C, (F) 750 °C, (G) 800 °C, (H) 850 °C, (I) 900 °C, and (J) 1000 °C. The vibrational peaks for forsterite were marked by open triangles, and for the new crystalline phase by solid ones. The open squares are for carbonates, and open circles for methoxides.

opened when carbon dioxide gas was used. First, a sharp, unsymmetric peak at 2347 cm^{-1} was observed, which was comparable to that of physically adsorbed carbon dioxide observed on the surface of magnesia.²⁴ Although the peak may be due to physisorbed carbon dioxide, the position and shape are quite different from that reported, probably because surrounding solid domain exerted some chemical interaction. The possibility of the peaks originated from physisorbed carbon dioxide was further eliminated by persistently observing the peak at 2347 cm^{-1} even after the powder was heated at 600 °C under vacuum ($\sim 10^{-3}$ torr) for 15h. Second, several peaks at 1542, 1456, 862, 714, and 429 cm^{-1} , were intensified after heating the xerogel at 600 °C in carbon dioxide. In an IR study of carbon dioxide adsorbed on mag-

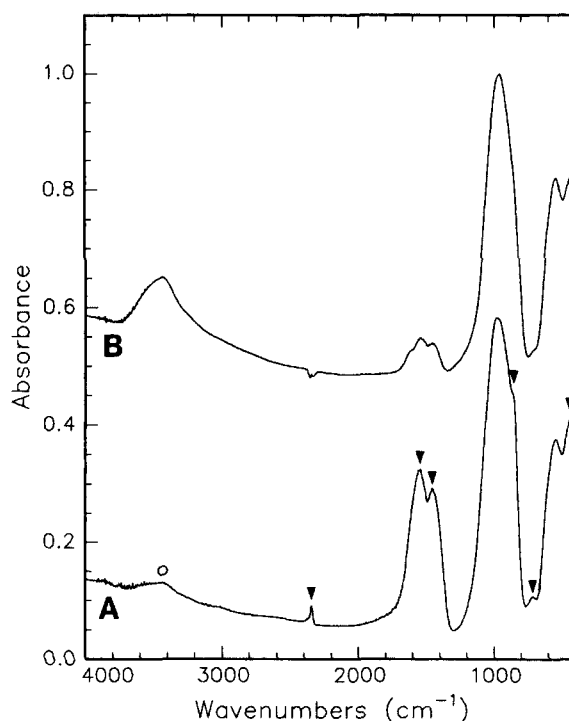
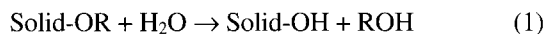


Figure 8. FTIR spectra of the forsterite xerogel heated at 600 °C, (A) in dry carbon dioxide, and (B) in humidified oxygen. The peaks marked by solid triangles are for unidentate carbonates. Open circle designates a broad peak for hydroxyl groups on surface.

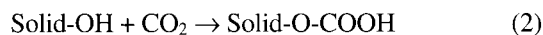
nesia, the broad peaks at 1510, 1390, 1035 (very broad), and 865 cm^{-1} were assigned to unidentate carbonate, which was generated by a reaction of adsorbed carbon dioxide and hydroxyl groups.²⁴ It was also speculated that the adsorbed carbon dioxide formed bidentate carbonate when water was not introduced and showed peaks at 1665, 1325, 1005, and 850 cm^{-1} . In the same study, the IR spectra of different types of carbonates adsorbed on various metal oxides were discussed. In general, the fundamentals ν_1 and ν_4 are separated by ~ 100 cm^{-1} for a unidentate complex, and by ~ 300 cm^{-1} for a bidentate complex. Also a peak was observed around 750 cm^{-1} for both types of carbonates. On the bases of these precedents, five peaks at 1542, 1456, 862, 714, and 429 cm^{-1} , from the xerogel heated in carbon dioxide at 600 °C are assigned to unidentate carbonates formed by the reaction between adsorbed carbon dioxide and hydroxy ligands. Significantly diminished -OH stretching vibration (bound OH groups) in the sample heated in carbon dioxide corroborates this suggested reaction pathway. Supporting this pathway, a large amount of carbon dioxide was immediately generated when the dark brown powder was mixed with dilute phosphoric acid, indicative of the existence of carbonate components in the sample.

In the case when carbon dioxide was used, it was observed that the humidity of the gas did not make difference in the crystallization. No matter whether the carbon dioxide was dry or humidified, only single phase of the 'pre-forsterite' was obtained at 800 °C. This observation strongly suggested that carbon dioxide acted as a major supplier of the carbon-

aceous component in the 'pre-forsterite', and that the residual alkoxides did not act as a major supplier. Water in the environmental gas facilitates further condensation in the xerogel, eliminating residual alkoxide groups by reaction (1) at low temperature.¹⁸



Therefore, when carbon dioxide was humidified, the residual alkoxides in the xerogel would be removed before the crystallization. If the residual alkoxides were major supplier of the carbon, the 'pre-forsterite' should not form in humidified carbon dioxide, which was not the case observed. This reasoning supports the generation of monodentate carbonates by the reaction (2) between carbon dioxides and surface -OH groups. Therefore, the porous nature of the xerogel also played an important role in allowing the access to hydroxyl ligands by carbon dioxide.



Incorporation of carbon containing species did not occur during pyrolysis of silica xerogels which did not contain magnesium. Facile formation of surface carbonates by a reaction between adsorbed carbon dioxide and surface hydroxy ligands has long been reported.^{24,25} Also, an inclusion of carbon impurities in single crystalline magnesia (MgO) during single crystal growth under a CO/CO₂ atmosphere has been reported.^{26,27} From these observations, it can be conceived that magnesium oxide moieties in the forsterite xerogel provided the incorporation sites to carbon. Therefore, it is crucial to distribute magnesium very homogeneously through the xerogel in order to obtain the 'pre-forsterite'.

In Figure 9, the PXRD pattern of the single phase product of the 'pre-forsterite' synthesized by heating the forsterite xerogel at 800 °C in carbon dioxide was compared to that of the single phase forsterite obtained by heating the xerogel in

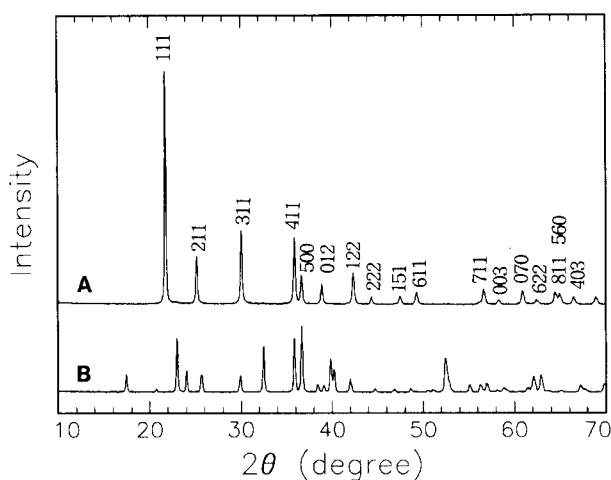


Figure 9. PXRD pattern of the new crystalline material (A), which was temporarily dubbed as 'pre-forsterite', obtained by heat treatment of forsterite xerogel in carbon dioxide at 800 °C. For comparison, the pattern of forsterite (B) obtained by heating the xerogel in humidified air was provided.

humidified air. It is apparent that only a single crystalline phase was formed when the xerogel was heated in carbon dioxide. Simultaneous development of more than one crystalline phase is unlikely considering that all the diffraction peaks appeared and disappeared simultaneously within same narrow temperature range of ~50 °C. The diffraction peaks at 30.0, 35.8, 36.6, 38.8, 44.3, and 58.3 °(2θ) are close to those of forsterite, but it was clearly shown that those diffractions do not belong to forsterite by previous high temperature XRD studies.²⁸ Basic calculation from the PXRD pattern suggested orthorhombic unit cell with the indices denoted in the Figure 9. Further refinement of information on the crystal structure of this new crystalline phase is on pursue.²⁹

The result of the elemental analysis on the 'pre-forsterite' was provided in Table 1. It was shown that the amount of carbon analyzed by combustion method roughly coincided with that analyzed from carbon dioxide generated in dilute acid. This observation strongly suggests that carbonaceous component in the 'pre-forsterite' is in the form of carbonate. Approximate mole ratios of carbon against magnesium and silicon were 1/8 and 1/4, respectively. Assuming the crystal structure of the 'pre-forsterite' is not much different from that of forsterite,²⁹ this mole ratio puts one carbon in one unit cell of forsterite. Assuming no defect, the empirical formula of the 'pre-forsterite' puts one carbon dioxide in one unit cell of forsterite; Mg₈Si₄O₁₆CO₂.

TG/DTA trace of the forsterite xerogel heated at a ramp of 10 °C/min in a flow of dry carbon dioxide is compared to that in humidified oxygen in Figure 10. In both cases, an initial weight loss of ~20%, accompanying an endotherm, was observed below 200 °C. This corresponds to the loss of physically adsorbed solvent, which occurred regardless of the kind of atmosphere used. Above 200 °C, the pattern of weight loss in carbon dioxide was very different from that in humidified oxygen. Major weight loss of ~15% occurred between 200 and 400 °C, and no further weight loss was observed until ~2% weight loss around 800 °C, in humidified oxygen. On the contrary, only ~5% weight loss occurred between 200 and 400 °C, and further weight loss of ~5% dragged on up to 750 °C, in carbon dioxide. Large weight loss of ~6.5% occurred between 750 and 800 °C, and an exotherm developed right after this weight loss. Since the exotherm developed after weight loss terminated, it is from crystallization process rather than from decomposition. Therefore, this exotherm at 800 °C corresponds to the crys-

Table 1. Results of the elemental analyses of the new crystalline material synthesized by heating the forsterite xerogel at 800 °C in carbon dioxide

Element	Analysis result (w%)	Error (w%)
Magnesium	35.78	±2
Carbon	2.17	±0.1
Hydrogen	Below limit	
Carbon (CO ₂)	2.26*	±0.05

*Carbon dioxide, which was generated when the sample was added to dilute hydrochloric acid solution, was analyzed by coulometric titration, and the result was converted to the theoretical amount of carbon.

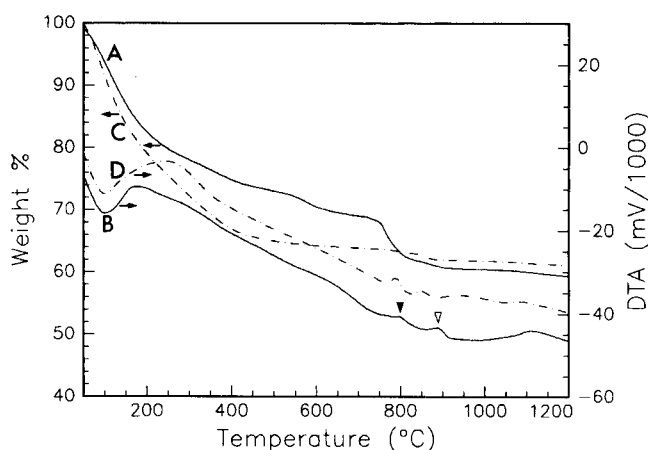


Figure 10. TG trace (A) and DTA curve (B) of a forsterite xerogel heated in a flow of dry carbon dioxide, compared to TG trace (C) and DTA curve (D) of the xerogel heated in humidified oxygen. The solid triangle marks the crystallization of xerogel into the new crystalline phase, 'pre-forsterite', and the open triangle denotes the phase transition from the 'pre-forsterite' to forsterite, accompanied by the expulsion of carbons from the crystalline lattice.

tallization of the 'pre-forsterite'. The PXRD and FTIR observations (see above) also conformed to the crystallization. This significant weight loss, which preceded the crystallization of the 'pre-forsterite', was not observed in air or oxygen, whether the gas was dry or humidified. By seeing the weight loss terminated before the crystallization, it was presumed that excess carbonates which did not fit to the crystal structure of the 'pre-forsterite' were eliminated below 800 °C. Corroborating to the reasoning, it was observed that those surface carbonate peaks at 1542, 1456 cm^{-1} were eliminated at 800 °C (Figure 7). A subsequent weight loss of ~2% occurred over ~90 °C above 800 °C until a second exotherm developed at 890 °C, which corresponded to the phase transition to forsterite. It was suggested that the carbonaceous component in the 'pre-forsterite' was removed before the phase transition.

On the bases of all the above experimental observations, the synthesis of the 'pre-forsterite' by heating the forsterite xerogel in carbon dioxide is conceptualized in Figure 11. Upon transforming alcogel into the xerogel, alkoxy ligands remained in the network structure of the xerogel. Obtaining compositional homogeneity at this stage was shown to be crucial in getting the new crystalline structure. By considering the major supplier of the carbonaceous component was carbon dioxide rather than alkoxide, it was suggested that the homogeneous distribution of magnesium was key factor, probably because carbonate would be bonded to magnesium rather than silicon. Upon being heated, some of those alkoxy ligands were removed by hydrolysis reaction, and the others were decomposed into carbonates. The weight loss of ~2% around 550 °C (in Figure 10) may be due to the decomposition of the alkoxy ligands. It was suggested that more carbonates were generated by the reaction between carbon dioxide and hydroxy ligands. Thereby, carbonaceous component, most probably carbonates bonded to magnesium

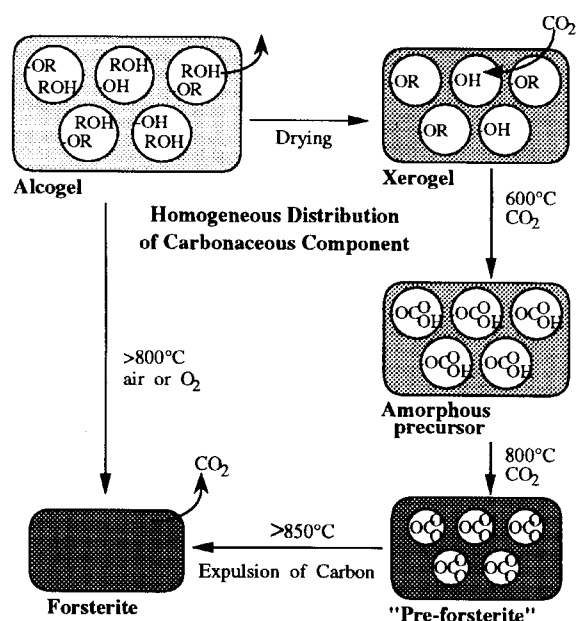


Figure 11. The crystallization of forsterite xerogel in carbon dioxide was chronically conceptualized by schematic diagrams.

sites, started fitting into the structural development around 600 °C. As local structure around metal centers started setting into the structure of the 'pre-forsterite' at 750 °C, unnecessary carbonaceous constituents were removed from the sample, and it crystallized into the 'pre-forsterite' at 800 °C. As the temperature was raised above 850 °C, the carbonaceous component was eliminated from the 'pre-forsterite', and phase transition turned the 'pre-forsterite' into forsterite above the temperature.

Conclusion

A new crystalline material having a composition similar to forsterite and including carbon in relatively high concentration was prepared by heating a forsterite xerogel, synthesized *via* the H_2O_2 -assisted sol-gel method, at 800 °C in an atmosphere of carbon dioxide. The powder X-ray diffraction pattern of this new crystalline material does not match that of any known compound. The composition of this new crystalline material is approximately $\text{Mg}_8\text{Si}_4\text{O}_{16}\text{CO}_2$, which is comparable to adding one carbon dioxide (as a form of carbonate) to one unit cell of forsterite. The carbonaceous component was incorporated in the amorphous xerogel around 600 °C as unidentate carbonates which were generated by reaction of carbon dioxide and hydroxyl ligands on magnesium oxide moieties of the sample. The crystallization of the new material at 800 °C was preceded by decomposition of most of these carbonates around 750 °C. This crystalline material was only stable below 850 °C, and irreversibly transformed to forsterite with concurrent expulsion of carbon at temperature higher than 850 °C. It appeared that this crystalline phase was a kinetic product which became stable by inclusion of carbon.

Experimental evidences indicated that carbon had to be

distributed very homogeneously through the sample, which suggested that the compositional homogeneity played a key role in obtaining the crystalline phase within a very narrow range of temperature, between 750 and 850 °C. For magnesiumsilicates, it would not be possible to reach this high level of compositional homogeneity by any other synthetic process, but the H₂O₂-assisted sol-gel route. The xerogel prepared by the method also has porous nature, rendering the access by carbon dioxide all over the sample much easier than in any other form of the precursor. The effect of the morphology of the xerogel on the crystallization process in carbon dioxide is being studied.

Acknowledgement. D. G. Park acknowledges the support by Korean Science and Engineering Foundation (K-N96048) with gratitude.

References

1. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science-The Physics and Chemistry of Sol-Gel Processing*; Academic: San Diego, USA, 1990; p 2.
2. West, A. R. *Solid State Chemistry and Its Application*; John Wiley & Sons: New York, USA, 1984; p 5.
3. Park, D. G.; Burlitch, J. M. *Chem. Mater.* **1992**, *4*, 500.
4. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science-The Physics and Chemistry of Sol-Gel Processing*; Academic: San Diego, USA, 1990; p 787.
5. Russo, R. E.; Hunt, A. J. *J. Non-Cryst. Solids* **1986**, *86*, 219.
6. Kang, J.; Park, S. H.; Kwon, H. Y.; Park, D. G.; Kim, S. S.; Kweon, H.-J.; Nam, S. S. *Bull. Korean Chem. Soc.* **1998**, *19(5)*, 503.
7. Burlitch, J. M.; Beeman, M. L.; Riley, B.; Kohlstedt, D. L. *Chem. Mater.* **1991**, *3*, 692.
8. Brindley, G. W.; Hayami, R. *Philos. Mag.* **1965**, *12*, 505.
9. Kazakos, A.; Komarneni, S.; Roy, R. *Mater. Lett.* **1990**, *10(9)*, 405.
10. Livage, J.; Henry, M.; Sanchez, C. *Progress in Solid State Chemistry* **1988**, *18*, 259.
11. Deer, W. A.; Howie, R. A.; Zussman, J. *Rock-Forming Minerals Vol.1-Orthosilicates*; Halsted, New York, USA, 1982.
12. Park, D. G.; Burlitch, J. M.; Geray, R. F.; Dieckmann, R.; Barber, D. B.; Pollock, C. R. *Chem. Mater.* **1993**, *5*, 518.
13. Park, D. G.; Higuchi, M.; Dieckmann, R.; Burlitch, J. M. *Bull. Korean Chem. Soc.* in press.
14. Werner, P. *Treor (calculation program)*; University of Stockholm: Stockholm.
15. Voronkov, M. G.; Mileshkevich, V. P.; Yuzhelevski, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, USA, 1978.
16. Yeager, K. E.; Burlitch, J. M.; Loehr, T. M. *Chem. Mater.* **1993**, *5*, 525.
17. The study on the effect of the xerogel morphology on the structural evolution during heat-treatment is on our pursue.
18. Park, D. G.; Duchamp, J. C.; Duncan, T. M.; Burlitch, J. M. *Chem. Mater.* **1994**, *6*, 1990.
19. Tarte, P. *Spectrochimica Acta* **1963**, *19*, 25.
20. Paques-Ledent, M. T.; Tarte, P. *Spectrochimica Acta* **1973**, *29A*, 1007.
21. *Powder Diffraction File*; McClune, W. F., Ed.; JCPDS Int. Center for Diff. Data: Swathmore, PA, USA, 1980.
22. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science-The Physics and Chemistry of Sol-Gel Processing*; Academic: San Diego, USA, 1990; p 160.
23. Millikan, J.; Keller, T. M.; Baronavski, A. P.; McElvany, S. W.; Callahan, J. H.; Nelson, H. H. *Chem. Mater.* **1991**, *3*, 386.
24. Evans, J. V.; Whateley, T. L. *Trans. Faraday Soc.* **1967**, *63*, 2769.
25. Gregg, S. J.; Ramsay, J. D. *J. Chem. Soc. (A)* **1970**, 2784.
26. Freund, F. *J. Crystal Growth* **1986**, *75*, 107.
27. Freund, F. *Phys. Chem. Minerals* **1987**, *15*, 1.
28. Park, D. G.; Martin, M. H. E.; Ober, C. K.; Burlitch, J. M. *J. Am. Ceram. Soc.* **1994**, *77(1)*, 33.
29. From many unpublished circumstantial evidences obtained by authors: will be described in separate article.