Acknowledgment. We thank Dr. S. Jansen for helpful discussions regarding the ESR measurements. This work was supported in part by the National Science Foundation, Ceramics and Electronic Materials, Division of Materials Research, under Grant No. DMR87-03526. The XRD measurements at University of Pennsylvania were performed by using central facilities of the Laboratory for Research on the Structure of Matter, supported by the National Science Foundation Grant No. DMR MRL 88-19885.

Low-Temperature Syntheses of Olivine and Forsterite Facilitated by Hydrogen Peroxide

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The use of an iron carbonyl, in combination with metal alkoxides, produced a new route to precursors for olivine ($(Mg_{0.9}Fe_{0.1})_2SiO_4$, Fo_{90}). The principal iron-containing intermediates, pentacarbonyliron and a low-valent, anionic metal carbonyl, produced by the reduction of $Fe_2(CO)_9$ by magnesium metal and $Mg(OMe)_2$ in the presence of $Si(OEt)_4$, were soluble in methanol. The iron-containing components were smoothly incorporated into the sol when the mixture of alkoxides was simultaneously hydrolyzed and condensed by the addition of aqueous hydrogen peroxide. H_2O_2 served at least two important functions: (1) it sequestered magnesium, thereby preventing precipitation of magnesium hydroxide; (2) it partially oxidized the iron carbonylate intermediates. After calcination, firing of pre-Fo_{90} powders at 1200–1300 °C in a CO/CO_2 atmosphere readily converted them to single-phase, crystalline olivine. Hot-pressing the resulting powder gave fine-grained, dense, solid specimens. DTA data and separate firings in an atmosphere of H_2 and CO_2 demonstrated that firing temperatures as low as 850 °C were sufficient to produce crystalline olivine. Without iron, synthetic forsterite, Mg_2SiO_4, was the sole product in a process that required no added strong acid or base as a catalyst for hydrolysis of $Si(OEt)_4$. Calcined forsterite precursor powders were converted to single-phase forsterite that was partially crystallized at 750 °C and fully crystalline at 1000 °C.

Introduction

The importance of magnesium and iron silicates predates recorded history; major components of the earth's upper mantle are aggregates or composites that contain these ceramic materials. Consequently, the study of their mechanical behavior is of considerable importance because many geological processes, involving movement of these materials, depend on their rheological properties.[1] Synthetic samples of such aggregates are needed for mechanical properties' measurements because (i) natural materials have uncontrollable amounts of various other components and (ii) fine-grained rocks, which are required to investigate deformation via diffusion mechanisms, are not available at the surface of the earth. Classical "crush and grind" ceramic methods have been used to the production of synthetic iron- and magnesium-containing silicates;[2–4] many processes have used high-pressure conditions to avoid the segregation of iron oxides and silica.[5,6] The "gel process", which consists of mixing alcoholic solutions of metal salts (e.g., nitrates) with silica (e.g., colloidal Ludox or hydrolyzable tetraethyl orthosilicate, TEOS) and then allowing the mixture to gel, has been used for the preparation of various synthetic silicate minerals,[7,8] including synthetic oxides of the type MgO, SiO_2, and Fe_2O_3; in the last-named case, however, evidence for the phase(s) produced was not given.[5] Recently, the preparation of olivine from silica (Nyacol), magnesium nitrate, and iron sulfate was described, but the low melting point of magnesium nitrate greatly complicated an attempt to spray-dry the precursor mixture.[6]

Thus, a new approach to the synthesis of olivine was needed, one that would enable formation of powders or gels directly from reaction mixtures while avoiding the use of metal salts that would either precipitate during reaction or complicate the drying step. This paper describes the preparation of olivine ($(Mg_{0.9}Fe_{0.1})_2SiO_4$, Fo_{90}), from metal alkoxides and an iron carbonyl. Although transition-metal carbonyl compounds have been used for the preparation of metal silicides,[9] we know of no report of such organometallics being used to prepare metal silicates. Without iron present, this new process also served as a low-temperature route to forsterite (Mg_2SiO_4, Fo_{100}), the end member of the olivine series. Forsterite has been prepared by firing mixtures of the component oxides, by coprecip-

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itation of hydroxy oxides in aqueous ammonia starting from magnesium amylate and TEOS,[10] by addition of magnesium acetate to partially hydrolyzed TMOS solutions in alcohol,[11] and recently from magnesium nitrate through "nanocomposite sol-gel processing".[12] It has been used for protective coating of steel.[13]

Experimental Section

General Comments. Most precursor synthesis operations were carried out under a dry argon atmosphere.[14] Reagent-grade methanol was distilled from magnesium methoxide. $Fe_2(CO)_9$ was prepared as described by King.[15] TEOS and $Bu^n{}_4NOH$ were obtained from Aldrich Chemical Co. Magnesium (99.99%) was obtained from Alfa Chemicals. All other chemicals were reagent grade. A Mattson Polaris IR-10410 spectrometer was used to record IR spectra of solutions in a sealed cell with CaF_2 windows.[16] Particle size distributions were obtained on ultrasound-treated suspensions in methanol by means of a Brinkmann Model 2010 analyzer. DTA measurements were made with a Perkin-Elmer Model 1700 instrument equipped with a Model 3700 data station and Model 7/4 controller; the gas flow rate was 35–40 mL/min; alumina was the reference material. X-ray diffraction patterns were obtained with a Scintag PAD V instrument. UV-vis spectra werre recorded with a Hewlett-Packard 8450A spectrometer.

Synthesis of Precursors. (1) For Olivine. *Caution: due to the formation of two toxic intermediates, TMOS*[17] *and pentacarbonyliron, this reaction should be conducted in a good fume hood.* To a mixture of TEOS (20.328 g, 0.097 57 mol) in 175 mL of methanol, in a dry 250-mL Schlenk reaction vessel (SRV) that contained a magnetic stirring bar, was added magnesium turnings (4.269 g, 0.1756 mol). The vessel was equipped with a water condenser that was fitted with a three-way stopcock gas adapter, one side of which was vented into a hood via a Dry Ice-cooled trap. The mixture was stirred while being cooled in an ice water bath to moderate the vigorous reaction and to reduce volatilization of silicon alkoxides, until all of the metal dissolved and evolution of hydrogen gas ceased (ca. 5 h). To the slightly cloudy solution was added $Fe_2(CO)_9$ (3.549 g, 0.009 757 mol). The mixture was stirred for 45 min, during which the solid dissolved, forming a deep reddish brown solution that became deep burgundy-colored upon standing for ca. 12 h. IR spectroscopy showed that pentacarbonyliron (ν_{CO} 2022, 2000 cm^{-1}; lit.[18] ν_{CO} in C_6H_{12} 2022, 2000 cm^{-1}) was a major component of the mixture (see Figure 1a).

The solution was decanted from a small amount of light-colored solid into a 2-L, three-necked, creased flask that was equipped with a mechanical stirrer (with a Teflon paddle) and with a water-cooled reflux condenser vented to the hood via a Dry Ice-cooled trap. To the rapidly stirred solution was added over 40 h a solution of 3.32 g (0.293 mol) of 30% H_2O_2 and 7.5 g (0.417 mol) of distilled water in 200 mL of reagent grade methanol by means of a 500-mL, non-pressure-compensating, addition funnel that was vented to the atmosphere by a drying tube. By means of a needle valve attached to the Dry Ice cooled trap, dry air was slowly drawn through the vessel, via the addition funnel, for 12 h. After ca. 4 mL of light yellow liquid was transferred from the cold trap to the reaction vessel by means of a syringe; the clear, amber mixture was stirred, purged with air, and irradiated by a 140-W Hanovia UV lamp at a distance of 13 cm for 5 h. IR analysis of the light amber mixture showed that only 2.5% of the initially formed $Fe(CO)_5$ remained.

After 0.63 g (0.97 mmol) of a 40% aqueous solution of Bu_4NOH in 150 mL of methanol was added, with stirring, during 30 min, the mixture was stirred and heated at reflux for 22 h, in the middle of which the viscosity increased considerably. MeOH (200 mL) was added, and ca. 0.5 mL of pale yellow solution in the cold trap was returned to the reaction vessel. An IR spectrum of the yellow, slightly hazy, viscous mixture showed no absorptions in the 2000-cm^{-1} region and indicated that all of the carbonyl species had been consumed. GLC analysis of the colorless distillate in the cold trap revealed no TEOS or TMOS.

Following addition of methanol (250 mL), the mixture was suction-filtered through "qualitative" paper. From a dropping funnel, toluene (1 L) was added to the stirred mixture in a 4-L conical flask over 30 min, and the mixture was heated for 40 min. Once cooled, the thick, translucent suspension was centrifuged for 30 min at 1800 rpm in eight 200-mL portions. Each sediment was alternately suspended in a solvent by means of a high-shear stirrer and then centrifuged. The solvents used were the following: three 100-mL portions of toluene followed by three 100-mL portions of cyclohexane. The final translucent sediment was freeze-dried from cyclohexane (−195 °C) and yielded 13 g of light tan, fluffy powder that was calcined and fired as described below.

In two similar preparations, $Fe_2(CO)_9$ was added prior to formation of the magnesium methoxide. In one reaction, conducted in 850–900 mL of methanol in a 2-L, three-necked flask on a reactant scale 2.45 times that described above, solid $Fe_2(CO)_9$ remained unreacted after complete dissolution of the magnesium metal at 0 °C. After the mixture had been warmed to room temperature and all of the solid had dissolved, the deep-burgundy colored solution gave the IR spectrum shown in Figure 1b. Heating at reflux in an O_2 stream for 40 h oxidized the iron completely. The second reaction was conducted at room temperature in a 250-mL SRV with 200 mL of methanol, on a reactant scale 0.3 times that described above; the IR spectrum of the reaction mixture is shown in Figure 1c. After slow addition of H_2O_2 (11.5 g) and H_2O (2 g) in methanol, complete oxidation of all metal carbonyl species in the reaction mixture required heating at reflux in an air purge for 2 h.

(2) For Forsterite from TEOS and Mg. To the vigorously stirred mixture of alkoxides, prepared from TEOS (21.19 g, 0.1017 mol) in 200 mL of methanol and magnesium (4.950 g, 0.2036 mol) in a 2-L, three-necked, creased flask, was added dropwise over 2 h a solution of 10.6 g (0.0935 mol) of 30% H_2O_2 in 200 mL of dry, distilled methanol, followed by a solution of 3.6 g (0.20 mol) of distilled, deionized water in 200 mL of dry methanol, added over 6 h. The nearly clear mixture was stirred and heated at a slow reflux for ca. 8 h and then was allowed to cool.

Working in the air, the thickened mixture was poured into a 2-L conical flask containing a 10-cm-long magnetic stirring bar. Toluene (600 mL) was added dropwise over 30 min, followed by a solution of $Bu^n{}_4NOH$ (0.015 g of 40% solution and 15 mL of MeOH). With the neck of the flask loosely covered, the mixture was stirred and heated to ca. 55–60 °C for 8–12 h. Once cooled, the thick, translucent suspension was centrifuged, washed with toluene and cyclohexane, and then freeze-dried as described above. The resulting fluffy white powder (20 g) was calcined and fired as described below.

(3) For Forsterite without H_2O_2: Coprecipitation. A solution of $Mg(OMe)_2$ (0.2258 mol) and TEOS (23.52 g, 0.1128 mol) in methanol (total volume 215 mL) was prepared by the procedure described in subsection 2. When only ca. 2.5 mL of a solution of 14.2 mL (0.79 mol) of distilled, deionized water in 225 mL of anhydrous methanol was added, dropwise, to the stirred solution of alkoxides over 1 h, a white precipitate formed. This precipitate dissolved completely upon addition of the remainder of the methanol and water solution to which had been added 25.8 mL (0.48 mol) of glacial acetic acid. The mixture was added, with stirring, to 500 mL of 1:10 aqueous ammonia in a 1-L creased flask over ca. 2 h. A white, finely divided precipitate formed immediately. Stirring was continued for 8 h, after which the suspension was heated to reflux and was stirred for 5 h. After having cooled,

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the milky white solid was collected from the suspension by centrifugation. The sediment was washed sequentially with dilute aqueous ammonia, methanol, and toluene before it was freeze-dried from cyclohexane, as described above. After the sediment was dried under vacuum at 100 °C, a white powder (15.9 g) was collected.

Powder Firing Techniques: (1) Olivine. The freeze-dried powder was calcined in air at 350 °C for 24 h to remove excess carbon, hydrogen, and water. To ensure that the partial pressure of oxygen, p_{O_2}, was within the oxygen stability field of Fo_{90},[19] a flowing mixture of CO and CO_2 was used inside of the furnace tube. High-temperature firing of the powder was done for 12 h at 1200 or 1300 °C with a p_{O_2} of 10^{-5} Pa in a high-purity, yttria-stabilized zirconia tube. The X-ray diffraction (XRD) pattern of the Fo_{90} is shown in Figure 3a.

Another sample of the precursor powder was calcined at 450 °C for 8 h and then was fired for two 8-h periods at 850 °C in an atmosphere of 9:1 H_2/CO_2 in a silica tube furnace. XRD analysis of the grey powder after each firing indicated a high degree of crystallinity and gave the pattern shown in Figure 3b.

(2) Forsterite. For DTA analysis, samples of the Fo_{100} precursor were heated to 1200 °C at 25 °C/h in air. The recovered DTA samples were single-phase forsterite, as determined by XRD analysis;[20] that from the sol–gel preparation was a white, friable powder, whereas the co-precipitated powder was well-sintered. Precursor powders (see subsection 2) were calcined under various conditions to optimize the conversion to forsterite. Powders were placed in a high-purity alumina crucible in a controlled-atmosphere furnace and were heated in an atmosphere of air or oxygen to the anneal temperature at a rate of 250 °C/h. The powders were held at temperature for 2 h and then were furnace cooled. The anneal temperature was varied from 500 to 1200 °C in 50 °C increments in an atmosphere of either air or oxygen. To make samples for hot-pressing, the fired powders were centrifuged in a vial containing methanol. The coarser grains were collected and were ground in an agate mortar and pestle. The centrifuge-grind cycle was repeated five times to produce the final powder.

Hot-Pressing Techniques: (1) Olivine. Powders were prepared for hot-pressing by grinding and centrifuging, as described above, and then were placed into nickel sleeves (1 cm long, 1.2-cm diameter) with a 1-mm-thick wall. The powder-filled sleeves were then placed into a hardened steel die. A close-fitting, hardened steel piston was used to compress the powder to stresses of about 320 MPa, by loading it with a hydraulic press. The sleeve was capped at each end with a nickel disk that was ca. 2.5 mm thick and that fit entirely into the sleeve. This design provided the maximum amount of contact area between the sleeve and the end caps, thereby creating a gas-tight seal at the ends of the sleeve as temperature and pressure were raised to hot-pressing conditions. With end caps in place, the sleeve containing the cold-pressed powder was slid into a 0.2-m-long iron jacket. The entire jacketed assembly was placed into the pressure vessel, where hot-pressing was accomplished using argon gas as the confining medium and a furnace mounted inside the pressure vessel.[21] Hot-pressing was done at 1250 °C under a confining pressure of 300 MPa for 3 h. Temperature and pressure were ramped up and down together, with temperature lagging pressure at the start of the run and pressure lagging temperature at the end. Temperature and pressure were ramped at rates of approximately 25 °C/min and 5 MPa/min, respectively. Once cooled, the jacketing material was removed from the jacketed sample by immersion in a 1:1 mixture of hydrochloric and nitric acids. A portion of the sample was then prepared for analysis with the optical microscope and the electron microprobe.

(2) Forsterite. All polycrystalline samples were isostatically hot-pressed in the apparatus described above. The forsterite was hot-pressed for 6 h at 1250 °C and 350 MPa in an iron sleeve.

Optimized Preparation of Forsterite without Bu^n_4NOH. Into a dry Schlenk tube capped with a septum was weighed TEOS (9.781 g, 0.04695 mol). Into a 1-L, creased, three-necked flask, equipped with a mechanical stirrer and a reflux condenser bearing a gas adapter was filtered a solution of $Mg(OMe)_2$ prepared, as described in subsection 1, from magnesium turnings (2.282 g, 0.093 89 mol) in distilled methanol (200 mL). To effect quantitative transfer, the SRV was rinsed with dry methanol (ca. 100 mL, transferred via a syringe), and the rinsings were added to the solution. Through a cannula, the previously weighed TEOS was quantitatively transferred into the flask with the aid of dry MeOH rinses (3 × 2 mL). While the mixture was stirred vigorously, a solution of 30% H_2O_2 (5.04 g, 0.044 mol; 0.284 mol of available protons) in ca. 100 mL of distilled MeOH was added, dropwise, over 7.5 h. This was followed by the dropwise addition of a solution of 1.80 g (0.10 mol) of distilled, deionized water in 100 mL of MeOH over a 7.5 h. The resulting, very slightly hazy mixture was stirred and heated to reflux by means of an electric heating mantle for 10 h and then was allowed to cool. After the moderately viscous sol was rotary evaporated under reduced pressure, the resulting, clear, glasslike gel was dried under a heat lamp for 2 h, ground to a powder in a mortar and pestle, and then dried in an oven at 100 °C for 8 h. The powder was calcined in a box furnace in air at 500 °C for 6 h, then heated to 1000 °C for 8 h, and furnace cooled. This gave 6.24 g (95% yield) of a white powder that was identified as forsterite by XRD (see Figure 8b).

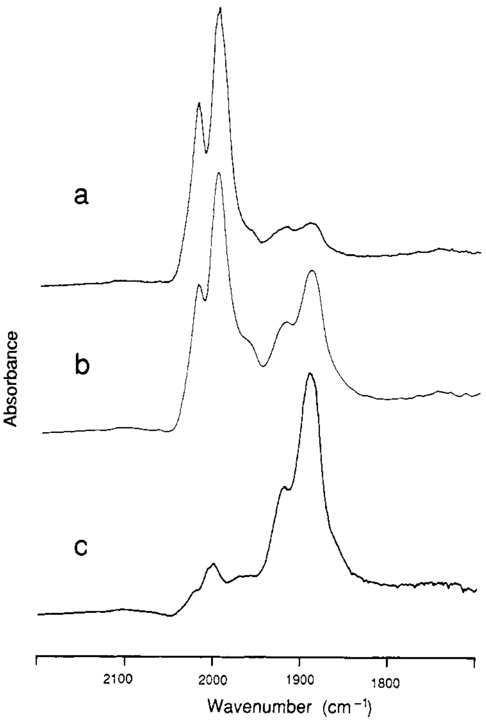

Figure 1. IR spectra of olivine precursor reaction mixtures prior to hydrolysis in which $Fe_2(CO)_9$ was added after (a) or before (b and c) formation of $Mg(OMe)_2$. See text for details.

In a second preparation, the sol (after having been heated to reflux) was spray-dried with a Brinkmann 190 instrument. The resulting white powder was heated to 650 °C at 100 °C/h, held at that temperature for 10 h, and then heated for ca. 20 h at 700 °C and at 725 °C for 17 h. XRD analysis of the white powder showed peaks for forsterite that were almost as narrow as those in Figure 8b.

Results and Discussion

Precursor Syntheses: (1) Olivine. As noted in the Introduction, segregation of iron was the most troublesome feature of previously reported sol–gel syntheses of magnesium–iron silicates. To address this problem, we started with iron in a low oxidation state which would be compatible with the other metal alkoxides present and with the water needed for their hydrolysis. We used diiron nonacarbonyl, $Fe_2(CO)_9$, because it is commercially available, has low volatility, is moderately stable, and, except for its toxicity, is easy to handle, i.e., can be weighed

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in air. $Fe_2(CO)_9$ generated soluble, iron carbonyl species, which, in the absence of air, were stable in the presence of the alkoxide(s). The iron-containing products that were obtained depended on the reaction conditions. When $Fe_2(CO)_9$ was added to $Mg(OMe)_2$ and TEOS in methanol, it was converted mainly to $Fe(CO)_5$, the IR spectrum of which (Figure 1a) contained bands at 2022 and 2000 cm^{-1}. On the other hand, when $Fe_2(CO)_9$ was present during the formation of magnesium methoxide (from magnesium metal), a highly colored iron carbonylate formed as the principal product, the IR spectrum of which (Figure 1c) contained bands at 1921 and 1892 cm^{-1} that were similar to bands at 1920 and 1852 cm^{-1} reported for $(Et_4N^+)_2Fe_2(CO)_8{}^{2-}$.[22] While several salts of $Fe_2(CO)_8{}^{2-}$ have been prepared and studied, no magnesium derivatives have been characterized.[23] During a large-scale preparation when the reaction mixture had to be cooled to moderate the reaction of magnesium and methanol and mixing of the heterogeneous reaction mixture was less efficient, intermediate amounts of $Fe(CO)_5$ and $Fe_2(CO)_8{}^{2-}$ were produced (see Figure 1b). In all cases, a cold trap was placed in the exit gas stream to prevent loss of the volatile byproduct, $Fe(CO)_5$. To ensure that the desired stoichiometry would be obtained, it was necessary to return this unwanted byproduct to the reaction mixture to force completion of the reaction.

Controlled hydrolysis of the alkoxides was carried out by slow addition of 30% hydrogen peroxide and water in methanol. As other experiments showed, (vide infra) aqueous hydrogen peroxide also prevented precipitation of magnesium hydroxide. Additionally, the use of 30% H_2O_2 without added water caused precipitation of a dark colored solid, the identity of which is under investigation. Complete oxidation of the iron carbonyl species was effected by exposure to dry air; progress of the oxidation reaction was monitored by IR spectroscopy. When large amounts of $Fe(CO)_5$ formed, a combination of UV irradiation and heating in air was used to oxidize it. In two preparations, a catalytic amount of strong base, $(Bu^n)_4N$-OH, was added ostensibly to help complete hydrolysis of the silicon alkoxides, but in a third, large-scale synthesis, none was used, and the product was identical with others prepared with the base.

Solvent was removed from the resulting pale yellow sols by either freeze-drying or spray drying. During the preparation for freeze-drying, the sol was caused to aggregate enough to permit collection by centrifugation by addition of toluene and by heating. During this process of changing solvents, the sediment (or its suspension) became clear and then turned translucent again. Clearing may be caused by the fortuitous matching of the refractive index of the particles with that of the solvent mixture. These observations suggest that the homogeneity of the particles occurs on a scale at least as small as the wavelength of visible light, (ca. 50 nm) since it is unlikely that we would have simultaneously matched the refractive indexes of two different compositions.[24]

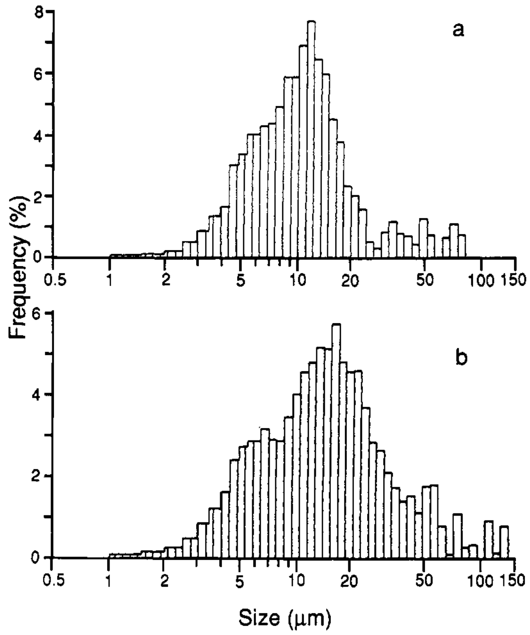

Figure 2. Particle size distributions of powdered precursors for (a) olivine and (b) forsterite.

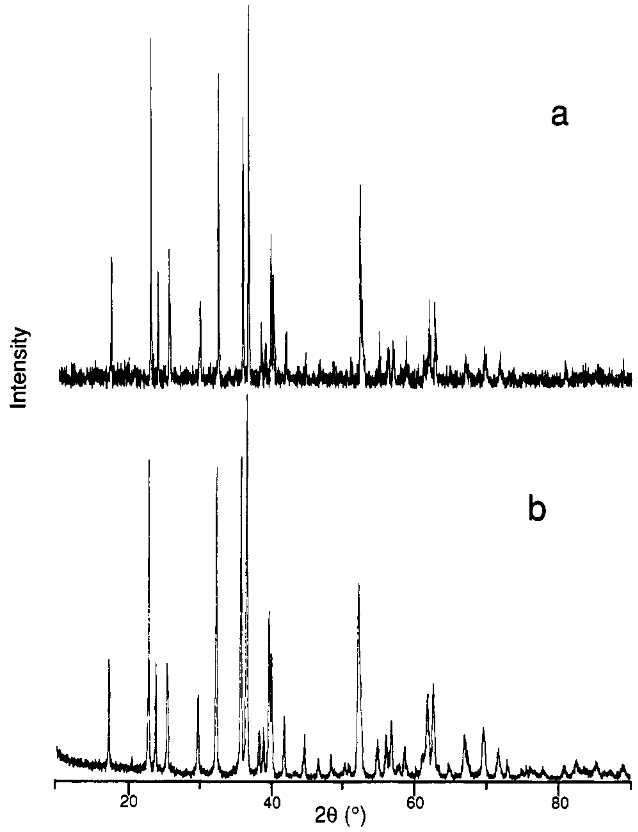

Figure 3. XRD patterns of olivines: (a) synthetic Fo_{90}, fired at 1200 °C in CO and CO_2; (b) synthetic Fo_{90}, fired at 850 °C in a N_2-diluted mixture of H_2 and CO_2.

When the sol was converted to a powder by the solvent change described above, followed by freeze-drying from a cyclohexane suspension, the particle size distribution of the resulting powder was fairly broad, and was centered about a mean of 10.2 μm (see Figure 2a). As shown by SEM, the olivine precursor powder contained many spherical particles less than 0.5 μm in diameter.

(2) Forsterite. We carried out similar preparations without an iron carbonyl to prepare single-phase, synthetic

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[24] The electronic spectrum of the clear, pale yellow sol in the methanol and toluene mixture was essentially featureless in the visible region but showed a tail of absorption into the UV region that started around 400 nm. While the very weak absorptions expected for iron(III) in the visible region of the spectrum were not observed under the conditions of the measurement,[25] further study of the nature of the iron species in the sol is in progress.

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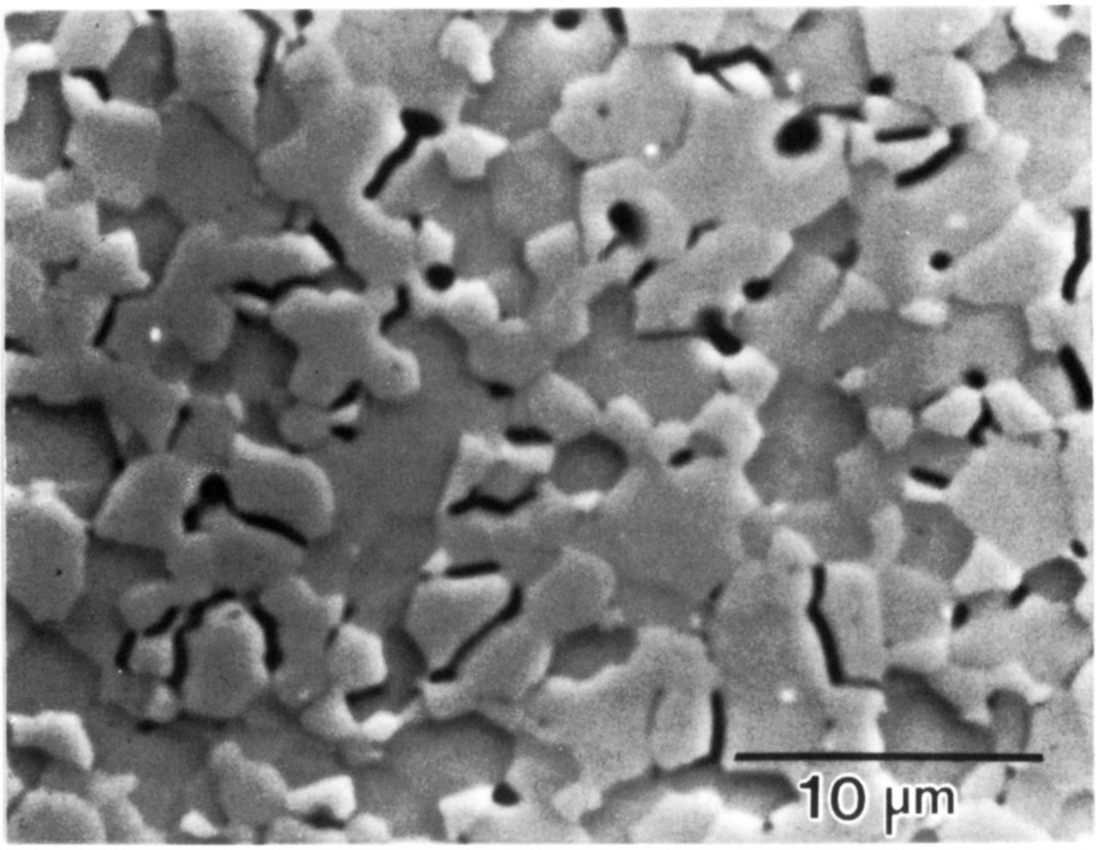

Figure 4. SEM back-scattered image of a polished and etched section of hot-pressed synthetic olivine. Intergranular cracks (dark lines) develop on cooling and depressurizing and are enlarged by subsequent etching.

forsterite.[26] In a separate study of the reactants, it has been learned that a catalytic amount of magnesium methoxide caused TEOS in methanol to rapidly convert to tetramethyl orthosilicate (TMOS) and ethyltrimethyl orthosilicate, as determined by gas chromatographic analysis of the vapors in the head space.[27] Thus, before any hydrolysis took place, TMOS had formed by a transesterification (alcohol exchange) reaction.[28] TMOS, therefore, was the principal silicon-containing reactant present in the forsterite precursor preparation and probably also in the olivine precursor preparation.[17] TMOS has been reported to hydrolyze more readily than TEOS.[29,30]

As with the olivine precursor preparation, aqueous H_2O_2 was used for hydrolysis and condensation. H_2O_2 has been used infrequently in the formation of ceramic materials: titania gels were formed from the reaction of H_2O_2 and titanium alkoxides;[31] niobium pentoxide gels were prepared by the destabilization of a hydrated niobium oxide sol with H_2O_2;[32] and residual organic components were removed from magnesium aluminate gels by treatment with H_2O_2.[33] In the present work, H_2O_2 played a novel role in both the forsterite and the olivine syntheses by preventing magnesium from precipitating as magnesium hydroxide, as happened when only water was added to a mixture of TEOS and $Mg(OMe)_2$ under the same conditions. The amount of 30% H_2O_2 used was such that approximately 50% of the alkoxy groups could be replaced by peroxo or hydroxo groups; it was assumed that both of the protons of H_2O_2 and one of the protons from H_2O were capable of reaction. Since the reaction of magnesium hydroxide with hydrogen peroxide has been widely used for the preparation of magnesium peroxide,[34] it is possible that either solvated MgO_2 or species containing the –MgOOMg– unit may be present in the reaction mixtures.[35]

To suppress gelation, aqueous H_2O_2 was diluted with methanol, and the concentration of TEOS was held at less than ca. 0.15 M at the end of the preliminary hydrolysis steps. Precipitation was avoided by very slow combination of the reactants and by efficient mixing. Subsequently, sufficient water was added to hydrolyze the remainder of the alkoxy groups. In other studies we have learned that a magnesium methoxide derived catalyst is responsible for not only the transesterification of TEOS but also for the facile hydrolysis and condensation of the resulting TMOS.[17] In early experiments, a catalytic amount Bu_4NOH was added just prior to isolation of the precursor

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[35] Iodometric titration of the precursor sol showed that at least 50% of the peroxide groups were still present after aggregation.[36] Such sols were capable of entering into other redox reactions, e.g., those with iron(II) complexes, to provide yet another new route to olivine.[37] The chemical species responsible for holding magnesium in solution, and their redox reactions are currently under study.

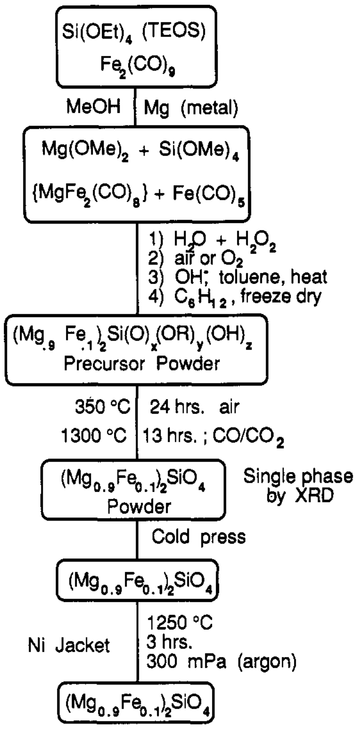

Figure 5. Schematic outline of the preparation of synthetic olivine specimens.

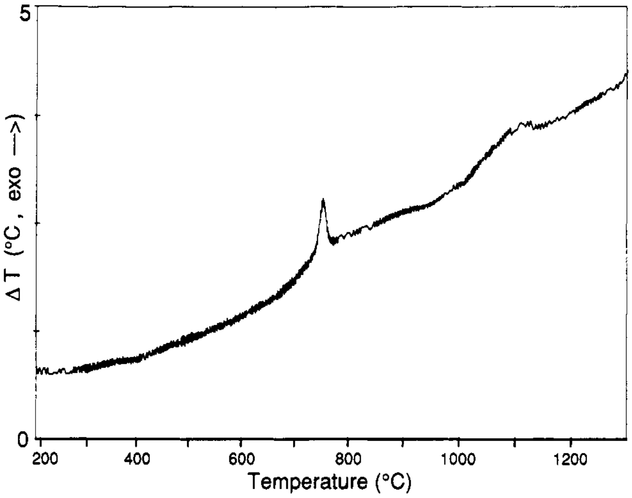

Figure 6. DTA scan (10 °C/min) of synthetic olivine precursor in a (9:1) H_2 and CO_2 atmosphere.

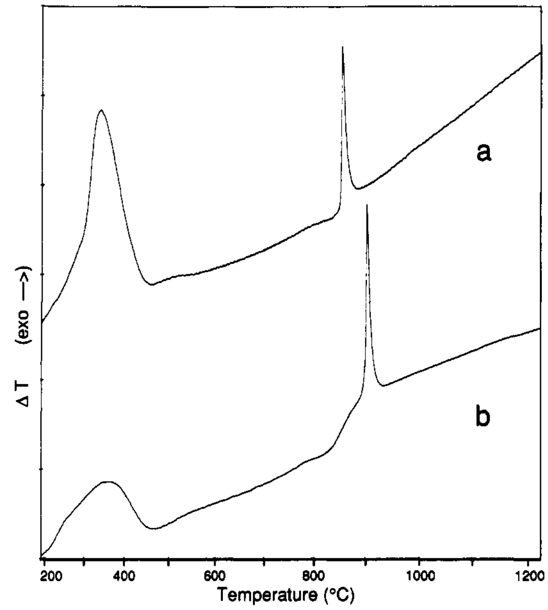

Figure 7. DTA scan (25 °C/min) of freeze-dried, synthetic forsterite precursors prepared by different methods: (a) sol–gel, and (b) coprecipitation.

to ensure completeness of condensation, but as shown by syntheses of forsterite precursors without added strong base and by the efficacy of the recently discovered magnesium methoxide derived catalyst, generated in situ,[17] the use of Bu_4NOH was unnecessary.

The resulting sol, which also has been used to form coatings on various substrates,[26,38] was converted directly to powder form by freeze-drying, by spray drying, or indirectly by gel formation. The bimodal distribution of particle sizes in the freeze-dried powder was broad (see Figure 2b) and was centered about a mean of 19.8 μm. Iodometric titration of a similarly prepared and freeze-dried forsterite precursor powder revealed that at least 35% of the initial peroxide content was retained in the dry product.[36] In the olivine preparation it is likely that some of this oxidation capacity may have been consumed in redox reactions with the low-valent iron components.

For comparison of the high-temperature processing characteristics with the sol–gel forsterite precursor, a coprecipitated precursor was prepared; magnesium acetate was formed in situ (from magnesium methoxide and acetic acid) and along with TEOS was rapidly hydrolyzed by addition of the mixture to aqueous ammonia.

Ceramic Formation and Characterization: (1a) Olivine (High Temperature Processing). After calcination at 350 °C in air to remove most of the organic residues, the precursor powder was fired at 1200 or 1300 °C in a CO/CO_2 mixture and gave single-phase olivine, identified by comparison of the XRD pattern (see Figures 3a) with that of natural, San Carlos olivine. The reducing atmosphere was needed to control the partial pressure of oxygen and ensure that iron was present as Fe(II). The fired powder was cold-pressed into a metal sleeve held in an iron jacket and piston assembly. The iron jacket isolated the sample material from the confining medium such that the sample as a whole was subjected to a hydrostatic pressure. Without the jacket, the gas would penetrate between each grain of the green body, thereby preventing neighboring grains from being pressed together. To buffer the sample at a p_{O_2} of 10^{-2} Pa, the jacketed pellet was hot-pressed in a nickel sleeve; the p_{O_2} throughout the sample was assumed to be determined by the metal–metal oxide (i.e., Ni–NiO) buffer of the jacketing material. Hot-pressing was done at 1250 °C under a confining pressure of 300 MPa for 3 h. This time was judged to be adequate because point defect relaxation times are less than 1 h at 1250 °C for the 0.8 cm^3 polycrystalline samples used.[39,40] The product was a fine-grained (5-μm average particle size) olivine ceramic as shown in Figure 4.[6] No secndary phases were seen, and within the accuracy of EDS analysis the stoichiometry was that of Fo_{90}. The overall process for the production of the dense olivine sample is

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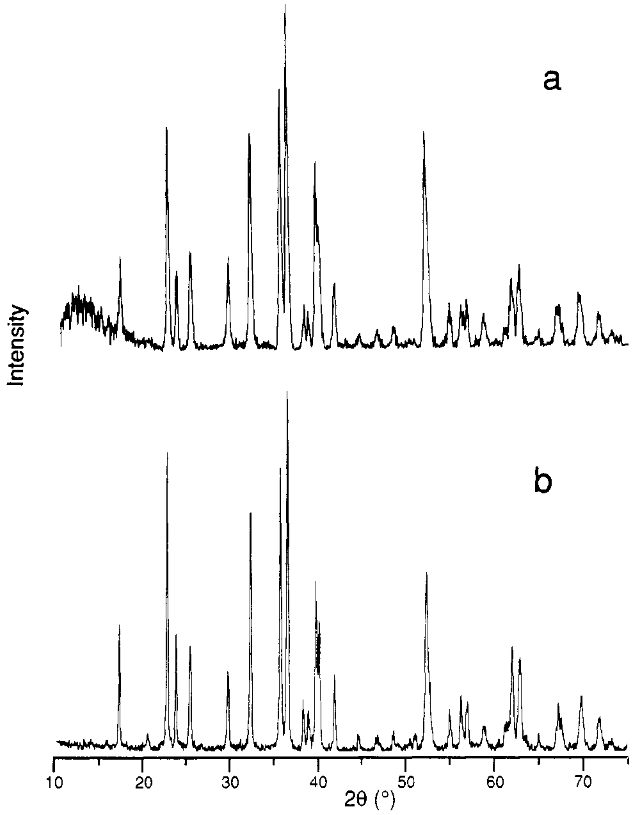

Figure 8. XRD pattern of synthetic forsterite fired at 1000 °C, prepared with added Bu^n_4NOH (a) and without Bu^n_4NOH (b).

shown schematically in Figure 5.

(1b) Olivine (Lower Temperature Processing). A DTA scan of a calcined Fo_{90} precursor powder in an atmosphere of 90% H_2 and 10% CO_2 showed a sharp exotherm at 750 °C and a broader one at ca. 1100 °C (see Figure 6). On a preparative scale, firing a sample in a N_2-diluted, H_2/CO_2 atmosphere at 850 °C for 8 h was sufficient to form crystalline olivine, as revealed by XRD analysis (see Figure 4b). The absence of peaks for other phases leaves little doubt that olivine had formed at the remarkably low temperature of 850 °C.

(2) Forsterite. Differential thermal analysis was used to characterize the decomposition reaction of the forsterite precursors (sol-gel and coprecipitated). The trace of the sol-gel precursor (Figure 7a) showed major exothermic events (peaks) at 350 and 850 °C. Results for the coprecipitated powder were similar (Figure 7b) with major exothermic events at 260, 375, and 910 °C. The DTA results indicate that the sol–gel prepared Fo_{100} crystallized at ca. 60 °C lower than the coprecipitated material; this is the lowest reported crystallization temperature for forsterite of which we are aware.

The short-term firing of larger samples heated at a rate of 250 °C/h required somewhat higher temperatures than that shown by the DTA peaks; XRD analysis showed that the sol–gel-prepared forsterite precursor completely crystallized after 2 h at 1000 °C as shown in Figure 8a. Synthetic forsterite gel precursors, prepared without addition of Bu^n_4NOH and by rotary evaporation of the solvent, showed, as expected, a very high degree of crystallinity after being fired at 1000 °C for 8 h (see Figure 8b).[41]

The microstructure of hot-pressed synthetic forsterite showed relatively little porosity and a mean grain size on the order of 5 μm. The material was single phase within the resolution of the electron microprobe.

Conclusions

$Fe_2(CO)_9$, in combination with metal alkoxides, produced a new route to precursors for olivine, Fo_{90}. The relative amounts of the principal iron-containing intermediates, pentacarbonyliron and a iron carbonylate, probably $[Fe_2(CO)_8]^{2-}$, varied with the reaction conditions; formation of the latter was favored by efficient mixing of $Fe_2(CO)_9$ with magnesium metal and by minimal cooling during the formation of $Mg(OMe)_2$. The carbonylate was the more useful on account of its low volatility and the ease with which it was oxidized. Without iron, a precursor for synthetic forsterite was prepared in an analogous process that required no added strong acid or base as a catalyst. Hydrogen peroxide served at least two important functions: (1) it sequestered magnesium, thereby preventing precipitation of magnesium hydroxide; (2) it partially oxidized the iron carbonyl intermediates.

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(41) The ease with which the Fo_{100} precursor crystallized was exemplified by our difficulty in keeping it amorphous during calcination; a spray-dried sample developed considerable crystallinity when kept in air at 700–725 °C for ca. 2 days. At these low temperatures, pure white, ceramic products were more readily obtained from low-density, freeze-dried powders than they were from their spray-dried counterparts.