

Sol-Gel Synthesis of Chromium-Doped Forsterite

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Received November 12, 1992. Revised Manuscript Received January 25, 1993

Pale purple, polycrystalline, chromium-doped forsterite powder was prepared at low temperature from a magnesium silicate sol. The chromium dopant, introduced as either chromium(II) acetate or chromium(VI) oxide, was combined in solution to maximize homogeneity. Electronic absorption spectroscopy indicated dopant ions, Cr^{III} and Cr^{VI} , were intimately bound to the magnesium silicate network. At a Cr/Si mole ratio of 0.04 or less, the dried xerogel formed only a single phase, forsterite, after calcination in humid air to 560 °C, and was fully crystalline above 800 °C. The residual carbon content of the xerogel was decreased by the use of humidified air during calcination. FTIR spectroscopy indicated that the dopant occupied both octahedral and tetrahedral sites. In the first attempts to grow single crystals of chromium-doped forsterite, coarse-grained samples were obtained by melting and solidification of the polycrystalline powder under an oxygen atmosphere by the crucible-free, floating zone method. Observation of a broad ESR peak for Cr^{4+} at room temperature and of typical near IR emission spectra indicated that the $\text{Cr}^{4+}/\text{Cr}^{3+}$ ratio in the melt grown samples was higher than that of commercial single crystals, grown under a more reducing atmosphere.

Introduction

Chromium-doped forsterite ($\text{Cr}:\text{Mg}_2\text{SiO}_4$) is a tunable, near-IR lasing material for which the lasing activity was first reported in 1988.¹ The emission is near 1.2 μm , which is amenable for use with fiber optic materials. There have been controversies over the identity and location of the lasing ions in the crystal.¹⁻⁴ Although the mechanism of lasing activity is not clear yet, it is generally accepted that Cr^{4+} in a "tetrahedral" site (replacing silicon) is the active center. Absorbing near the crystal's emission band, Cr^{2+} and ionic impurities such as Fe^{3+} ,² are known to deteriorate the quality of the laser.⁵ Recent studies suggest an interaction between Cr^{4+} and Cr^{3+} centers provide an excitation mechanism for the Cr^{4+} upper laser level,^{6,7} and decreasing the ratio of Cr^{4+} to Cr^{3+} would deteriorate the quality of the laser.⁷ These observations suggest that the way to improve the laser's performance is to increase the $\text{Cr}^{4+}/\text{Cr}^{3+}$ ratio and to eliminate absorptive impurity ions.

Forsterite has been prepared by conventional heat treatment of a mixture of metal oxides at 800–1525 °C with intermittent grindings,⁸ by coprecipitation,⁹ and by

several variations of the sol-gel route.^{10,11} Most single crystals of chromium-doped forsterite have been prepared by the Czochralski method (from a mixture of metal oxide powders), for which a reducing or slightly oxidizing atmosphere is used to protect the crucible from oxidation.¹² Under reducing conditions, the $\text{Cr}^{4+}/\text{Cr}^{3+}$ ratio is expected to be considerably lower than that possible under a highly oxidizing atmosphere. The laser pedestal growth method, for which no crucible is needed, has been used to grow forsterite crystals doped with chromium and aluminum under an oxygen atmosphere; the resulting crystals, however, were less than 2 mm in diameter and contained predominantly Cr^{4+} .¹³⁻¹⁵

To increase the size of the crystals grown in oxygen, we developed a sol-gel synthesis of $\text{Cr}:\text{Mg}_2\text{SiO}_4$ and have begun to use the floating zone method to grow single crystals from the resulting powder. This paper describes the synthesis of chromium-doped forsterite and first attempts to grow single crystals. Details of the growth of large single crystals will be reported elsewhere.

Experimental Section

General Comments. Magnesium turnings, 99.99%, were obtained from Alfa, and chromium pellets, 99.999%, were obtained from United Mineral & Chemical Corp. Tetraethylorthosilicate (TEOS), 99+%, was used as received from Aldrich. Magnesium oxide (MgO) powder, 99.999%, and chromium oxide (Cr_2O_3) powder, 99.999%, were obtained from Atomergic Chemicals Corp. Silicon dioxide (SiO_2), 99.995%, was obtained from Johnson Matthey Electronics. The metal oxide powders were

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–325 mesh (44 μm). Unless specified, all other chemicals were reagent grade. Powder X-ray diffraction patterns were obtained with a Scintag PAD X diffractometer. TGA was performed with a Du Pont TGA-951 Thermal Analyst 2000 thermogravimetric analyzer. A Mattson FTIR GL-4020 spectrometer was used to take IR spectra of powders in KBr pellets. UV-vis spectra were taken with a Hewlett-Packard 8451A diode array spectrophotometer or a Varian Cary-5 UV-vis-NIR spectrophotometer. Chromium analysis of single crystals was done with a JEOL Superprobe 733, Tracor Northern 5500. ESR spectra were taken with a Bruker ER 200 D-SRC spectrometer in X band. The surface area of the precursor powder was measured with Micromeritics' FlowSorb II 2300 using the BET method. SEM was done with a JEOL JSM-35 CF electron microscope.

Precursor Synthesis. All procedures that involved solutions were carried out under a dry and oxygen-free argon atmosphere.¹⁶ Methanol was degassed and distilled over $\text{Mg}(\text{OMe})_2$. Hydrolyzing agents (H_2O_2 and H_2O in MeOH) were added via cannula from a Schlenk tube that was pressurized by argon from a syringe in a syringe pump.

(a) *From Chromium(II) Acetate.* Chromium(II) acetate was prepared as described in the literature¹⁷ except for the use of Schlenk tube techniques.¹⁸ The UV-vis spectrum in MeOH (328, 485, and 350 nm, Figure 2a), was nearly the same as that reported for $\text{Cr}(\text{OAc})_2$ in EtOH.¹⁹

Into a 50-mL Schlenk reaction vessel (SRV), 28.331 g (0.1360 mol) of TEOS was transferred via a cannula under argon. A dry 1-L three-necked round-bottom flask equipped with a water-cooled condenser, which was connected to a source of argon via a three-way stopcock, was charged with magnesium (6.679 g, 0.2748 mol) and 600 mL of MeOH. After all the Mg reacted and gas evolution ceased, the solution was filtered through fritted filter tube (porosity "D"), into a 3-L round-bottom creased flask, equipped with a water condenser and a mechanical stirrer. The 1-L flask and the filter tube were rinsed with MeOH (3×50 mL). The TEOS in the 50-mL SRV was combined with the $\text{Mg}(\text{OMe})_2$ solution via a cannula and the SRV was also rinsed with MeOH (3×50 mL). The rinsings were added to the reaction mixture.

The well-stirred mixture was partially hydrolyzed by dropwise addition of 14.6 g of 30% H_2O_2 (0.129 mol of H_2O_2 and 0.569 mol of H_2O) in 300 mL of MeOH, during 33 h with vigorous stirring. No volatile species (TMOS, TEOS, etc.) remained, as determined by head-space analysis.²⁰ To eliminate any oxygen gas present, possibly formed by decomposing H_2O_2 , argon was bubbled through the clear sol with vigorous stirring for 7 h.

Into a 1-L round bottom flask, chromium(II) acetate (0.259 g, 1.38×10^{-3} mol) was dissolved in 300 mL of MeOH. The clear pink solution was added to the above sol via cannula during several minutes with stirring. The color of the clear sol turned greenish yellow upon addition of the acetate solution. The mixture was further hydrolyzed by addition of 4.92 g of deionized H_2O (0.27 mol) in 300 mL of MeOH added during 33 h with vigorous stirring. The clear, greenish yellow sol was heated at reflux for 12 h, which caused it to become much lighter in color. After the solvent was removed by heating (steam bath) during rotary evaporation under reduced pressure, the resulting transparent xerogel was reduced to a fine pale green powder by grinding with a mortar and pestle. About 30 g of dried precursor powder was prepared from 0.15 mol of TEOS.

Xerogels with several different chromium to silicon mol ratios (0.001–0.1) were prepared by the same general procedure except for the amount of chromium(II) acetate added.

(b) *From Chromium Trioxide.* To a mixture of 0.186 g (0.001 86 mol) of CrO_3 and 0.15 mL of deionized H_2O in a 100-mL SRV was added 100 mL of MeOH. Vigorous reaction began immediately. After the reaction ceased, the clear, dark red solution was combined with a mixture of TEOS (18.94 g, 0.0909 mol) and

$\text{Mg}(\text{OMe})_2$ (prepared from 4.42 g, 0.1818 mol of magnesium in 600 mL of MeOH, as described above) in a 2-L round-bottom creased flask.

The clear, brown solution was partially hydrolyzed by addition of a solution of 9.684 g of 30% H_2O_2 (0.0854 mol of H_2O_2 and 0.377 mol of H_2O) in 225 mL of MeOH, during 17 h with vigorous stirring. After the addition, the clear solution was much lighter in color. The sol was further hydrolyzed by addition of 3.36 g (0.187 mol) of deionized H_2O in 200 mL of MeOH, during 17 h. The clear yellow sol was heated at reflux for 7 h after which the color became pale greenish yellow. A fine, pale green powder was prepared by removal of the solvent as described in the previous section.

UV-Vis Spectroscopy. UV-vis spectra of reaction mixtures were obtained from samples transferred by a gastight syringe into a 1-cm silica cuvette equipped with a rubber septum and flushed with argon. After a portion of the sol was ultracentrifuged at 90 000 rpm for 40 min to precipitate polymeric species, a spectrum was taken of the clear supernatant liquid. The sol was reanalyzed after it had been aged in a tightly closed polyethylene bottle for 1.5 and 3.5 months. Spectra were also taken of a 1-mm-thick, yellowish green, transparent gel monolith, prepared by drying the freshly made sol in air over a period of 72 h, and of a thin slice of single-crystal forsterite cut in a random orientation and polished.

Heat Treatment of Xerogels. To evaluate the limit of dopant concentration, xerogels with different chromium contents, held in open fused silica tubes, were heated to 1000 °C at 100 °C/h in an air flow and held at that temperature for 4 h. The resulting pale purple powders were used for XRD and FTIR measurements.

The calcination characteristics of the xerogels were examined by TGA in two different gas media, one in dry air and the other in humid air (i.e., air partially saturated with water). Results of the thermal analyses were compared to those of an undoped forsterite precursor.²¹ For the purpose of comparison, the concentration of silicon was the same as that used for the doped precursor, and all sols were dried by rotary evaporation. The heating rate was 100 °C/h. The flow rate of the gas was 50 mL/min. "Dry" air was generated by passing Airco compressed air through a column of Mallinckrodt Aquasorb. "Humid" air was prepared by passing air through water via a fine fritted tube in a 1-L gas washing bottle.

To observe crystallization behavior, the xerogel that had a chromium-to-silicon mole ratio of 0.01 was heated successively at 500, 600, 700, 800, 900, and 1000 °C in air for 12 h at a ramp rate of 100 °C/h. IR spectra and X-ray diffraction patterns were taken from each sample. The size of the diffraction volume (crystallite size) was calculated by the Scherrer equation²² from the half-width of the (211) peak of chromium-doped forsterite (heated at 1000 °C) compared to the (111) peak of silicon powder (–325 mesh, Aldrich). Spectroscopic analysis (ICP-MS) showed 0.37% Cr.

To prepare powder for the feed rods needed for single-crystal growth by the floating zone method, the xerogel was preheated at 200 °C in a vacuum oven for 4–6 h; a flow of humid air was admitted through the vent valve of the oven to eliminate most of the organic residues. This precalcination step was accompanied by considerable shrinkage. The resultant powder was heated to 500 °C for 10 h and further heated at 1000 °C for 5 h under a flow of oxygen. Chromium-doped forsterite powder (19 g, 90% yield based on Si) was prepared from 0.15 mol of TEOS.

Single-Crystal Preparation. Growth of single crystals of chromium-doped forsterite was attempted by the crucible-free, floating zone method in a single ellipsoid mirror furnace^{23,24} from polycrystalline chromium-doped forsterite. Two kinds of feedstocks were tried: one was made from a mixture of metal oxides, and the other from the polycrystalline powder synthesized as described above. A mixture of oxide powders (MgO , SiO_2 , and

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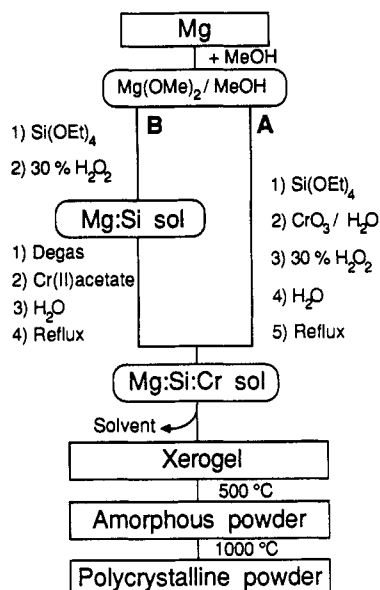


Figure 1. Schematic outline of the preparation of polycrystalline chromium-doped forsterite powder. The dopant was introduced as chromium(VI) trioxide (A) or as chromium(II) acetate (B).

Cr_2O_3 in a mol ratio of 2:1:0.02), was prepared by thoroughly mixing commercial powders.

Cold-pressed rods (10 mm diameter \times 40 mm long) were sintered in air for 3 h at 1300 °C; no binder or sintering aid was used. The rotating feed rod was melted in an oxygen atmosphere, at a total pressure between 2 and 4 atm by focused lamp radiation, and pulled down at 2 mm/h for slow cooling of the melt. The samples obtained in this way contained large crystalline grains of chromium-doped forsterite.

Chromium concentrations of the crystals obtained were determined by microprobe analysis (WDS). For XRD analysis, pulverized powder samples of the fused solids, grown from each type of feedstock, were prepared by vibratory milling in a tungsten carbide vial for 2 h.

ESR and Emission Spectroscopy. To assess the role of the highly oxidizing medium during the single-crystal growth experiment, ESR and emission spectra were taken from the single-crystalline grains of the sample.

Large grains from samples grown by the floating zone method were oriented by a real-time, Laue backscattering technique and were cut into several smaller pieces (e.g., $2 \times 4 \times 7$ mm). ESR spectra were taken at 9.4 GHz with a modulation amplitude of 100 kHz. A chromium-doped forsterite single crystal, purchased from Mitsui Mining Co., was also analyzed for comparison.

An argon ion laser was used to excite the chromium-doped forsterite at 514.5 nm for emission spectroscopic studies. A scanning monochromator measured the resulting fluorescence spectrum.

Results and Discussion

Synthesis. The published procedure for the preparation of forsterite, aided by H_2O_2 ,²¹ was modified for the introduction of the chromium dopant (Figure 1). The two main goals were to prepare a homogeneous precursor and to retain that homogeneity in the fired powder. To prevent gelation, the concentration of silicon was kept below 0.1 M. Hydrolyzing reagents, 30% H_2O_2 and water, were diluted before addition. All reagents were added very slowly, and the mixture was well stirred to minimize the local concentration of reagents. As observed previously,²¹ the use of H_2O_2 made it possible to carry out hydrolysis and condensation without precipitation of $\text{Mg}(\text{OH})_2$.

The chromium dopant was introduced either as the reaction product of chromic acid with MeOH ²⁵ or as chromium(II) acetate. Chromic acid, prepared by dis-

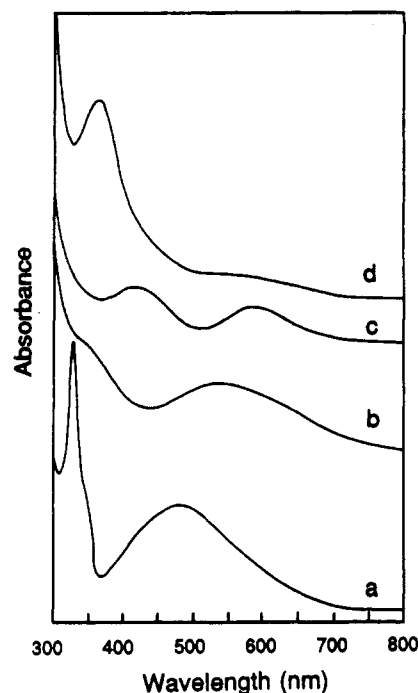


Figure 2. UV-vis spectra of (a) $\text{Cr}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$ in MeOH ; (b) reaction product of $\text{Cr}(\text{II})$ acetate and H_2O_2 in MeOH ; (c) product formed by exposing a methanolic $\text{Cr}(\text{II})$ acetate solution to air; (d) magnesium silicate sol, immediately after the addition of $\text{Cr}(\text{II})$ acetate. The absorbance scales for (a)–(c) were expanded relative to that of (d) for better comparison.

solving commercially available CrO_3 in a very small amount of water, reacted with MeOH forming a highly colored product that has been postulated to be a $\text{Cr}(\text{IV})$ complex.²⁵ The dark red solution was mixed with other starting materials, $\text{Mg}(\text{OMe})_2$ and TEOS. The color change of the reaction mixture upon hydrolysis, from dark brown to yellow and eventually to bright greenish yellow, occurred gradually. The bright greenish yellow color, caused by a broad absorption centered at 367 nm, developed after most of the H_2O had been added.

In contrast, $\text{Cr}(\text{II})$ acetate in MeOH was introduced after the sol was partially hydrolyzed by addition of 30% H_2O_2 . The amount of aqueous H_2O_2 was chosen to hydrolyze approximately 50–75% of the alkoxy groups. After all the H_2O_2 was added, the solution was colorless and clear. At this point, all the monomeric silicon alkoxides were hydrolyzed; no volatile species were present as shown by head-space analysis.²⁰

When the $\text{Cr}(\text{II})$ acetate solution was combined with the partially hydrolyzed, degassed sol in an oxygen-free environment, there was an immediate color change from pink to greenish yellow, indicating a change in the oxidation state of the chromium (see below). The color change was caused by a new broad absorption at 367 nm; no absorption for $\text{Cr}(\text{II})$ acetate was observed (Figure 2d).

The air-exposed solution of $\text{Cr}(\text{II})$ acetate in MeOH (Figure 2c) had a spectrum typical of a $\text{Cr}(\text{III})$ oxo compound in an octahedral environment,^{26–28} showing two broad absorptions at 415 and 518 nm. When the pink $\text{Cr}(\text{II})$ acetate solution was added to excess 30% H_2O_2 in

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MeOH, there was no color change for a few minutes and then, suddenly, it turned bluish purple (Figure 2b). This solution was stable in air and in the dark. In the light, it turned pale green and had the same absorption spectrum as that shown in Figure 2c, after a week. A reaction of Cr(II) acetate and free H_2O_2 in the sol is unlikely because the observed spectrum (Figure 2d) is quite different from the spectrum of their reaction product in MeOH (Figure 2b). Moreover, the product of the reaction of aqueous chromous perchlorate and H_2O_2 had an absorption spectrum²⁹ (similar to Figure 2c) typical of Cr(III) in an octahedral environment.³⁰ The above observations indicate that there was no free H_2O_2 remaining in the magnesium silicate sol. Although iodimetric titration of the undoped forsterite precursor sol has shown that at least 56% of the peroxide added was still present after 12 h,³¹ the sol's strongly oxidizing capacity was not due to free H_2O_2 . Although it is known that magnesium hydroxide³² and $\text{Mg}(\text{OMe})_2$ ³³ can react with hydrogen peroxide forming magnesium peroxide, recent work has shown that MgO_2 is not a likely component of the sol.³¹ A hydroperoxide of magnesium, which has been suggested as the active oxidant,³¹ would be expected to readily oxidize $\text{Cr}(\text{OAc})_2$ and possibly coordinate the resulting Cr complex to the magnesium silicate network.

The UV-vis spectra of the sols prepared from CrO_3 and $\text{Cr}(\text{OAc})_2$ were identical and were essentially unchanged by heating at reflux (Figures 2d and 3a). Both contained a strong absorption at 367 nm and weak absorptions at 415 and 570 nm. Chromate, i.e., Cr(VI), ion in aqueous solution and in the solid state has a characteristic absorption at 373 nm.^{34,35} The weak absorptions around 415 and 570 nm are typical d-d transitions for Cr(III) in an octahedral environment.³⁰ The strong peak at 367 nm is assigned to Cr(VI) in a tetrahedral environment, and the weak broad peaks at 415 and 570 nm are assigned to Cr(III) in an octahedral environment. The ratio of Cr(VI) to Cr(III) cannot be assessed quantitatively, because the molar absorptivities are unknown. A ratio of 0.6 can be estimated, however, because the molar absorptivity of the charge-transfer band in Cr(VI) compounds is about 2 orders of magnitude larger than that of the Cr(III) d-d transitions in most complexes. The spectrum of the sol heated at reflux (Figure 3a) is quite similar to that of a chromium-doped ZnAl_2O_4 xerogel heated at 750 °C, the peaks of which were assigned in same way; the spectrum of the unheated, chromium-doped ZnAl_2O_4 showed only two peaks for octahedral Cr(III).³⁶ The spectrum of a chromium-doped silica xerogel contained only peaks for Cr(III).³⁷

Given the known reactivity of Cr(VI) oxides with alcohol,²⁵ the existence of Cr(VI) in the chromium-doped magnesium silica sol is unusual. The Cr(VI) center may be attached to the magnesium silicate network upon

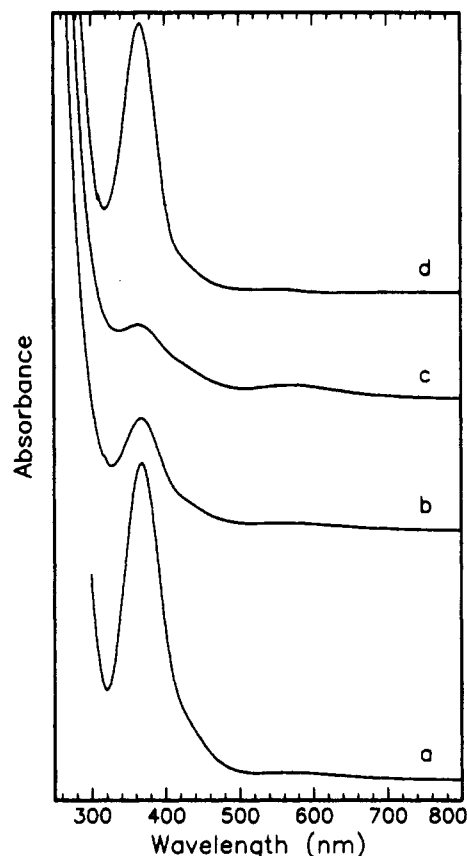


Figure 3. UV-vis spectra of chromium-doped magnesium silicate: (a) sol, immediately after being heated at reflux; (b) sol, after 1.5 months; (c) sol, after 3.5 months; (d) xerogel monolith, after 3.5 months.

oxidation by $-\text{Mg}-\text{OOH}$ groups³¹ and stabilized there by a large excess of the oxidant. Several observations corroborate this postulate. The UV-vis spectrum of the supernatant liquid of an ultracentrifuged sample of the sol, prepared from $\text{Cr}(\text{OAc})_2$, showed no peaks and indicated that all the chromium ions were in the sediment with the sol. Cr(VI) was generated instantaneously when Cr(II) was added to a magnesium silicate sol that already had all the strongly oxidizing sites formed. To verify the postulate that the Cr(VI) ions were stable in a metal oxide network, a dried xerogel monolith was made from a fresh sol immediately after heating at reflux. This monolith, which had little free methanol to react even if the Cr(VI) ions were released from the entrapped sites, was aged for 3.5 months before a UV-vis spectrum was taken. The sol from which the monolith was made was aged in a closed container for the same period. Spectra were taken after 1.5 (Figure 3b) and 3.5 months (Figure 3c). After 3.5 months, the ratio of Cr(VI) to Cr(III) did not change in the xerogel monolith (Figure 3d), whereas it decreased from 0.6 to approximately 0.03 in the sol (Figure 3c). In the sol, the Cr(VI) ions that may have been entrapped in the metal oxide network were gradually exposed to solvent by reesterification³⁸ and were slowly reduced by methanol to Cr(III). In the monolith the Cr(VI) ions were fixed in the rigid metal oxide network and could not be reduced by the small amount of residual MeOH.

After hydrolysis of the remaining ligands (about 25%) by addition of water, the sol was heated to accelerate

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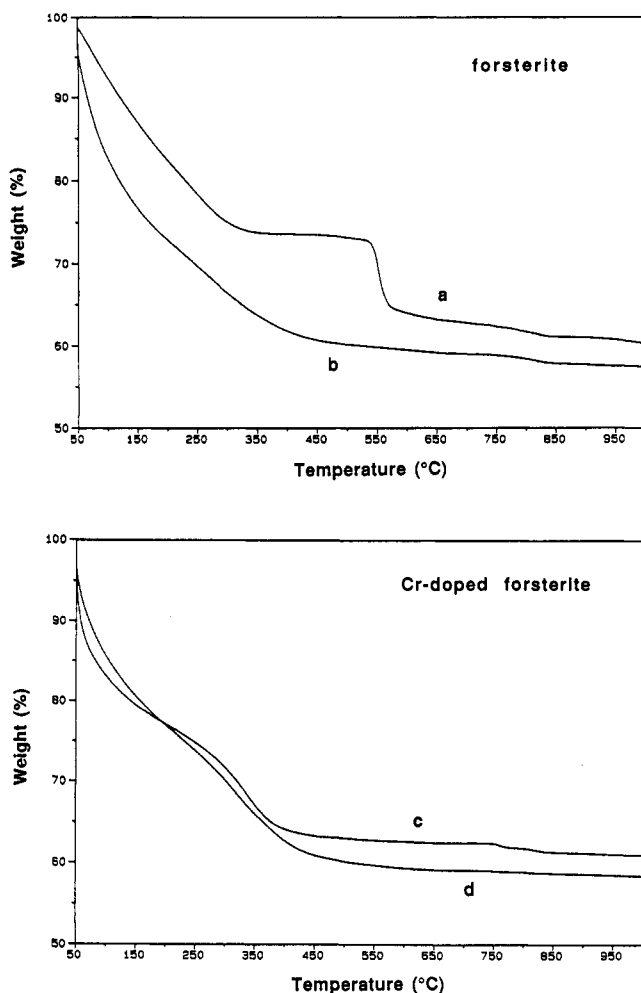


Figure 4. TGA traces of xerogels: (a) forsterite in dry air, (b) forsterite in humid air, (c) Cr-doped forsterite in dry air, (d) Cr-doped forsterite in humid air. The heating rate was 100 °C/h for all samples.

condensation reactions.³¹ The resulting transparent sol showed no tendency to form a gel or a precipitate.

Calcination. The greenish transparent xerogel, which formed upon removal of the solvent, was very brittle and was easily ground into a powder that consisted of irregular shapes from 0.1 to 10 μm (SEM). The xerogel had a lower surface area (4.5 m^2/g), measured by BET, and the surface area decreased further upon calcination. This low surface area is rather unusual for a silicate xerogel synthesized by the sol-gel method.³⁹

Compared with the pure undoped forsterite, the chromium-doped forsterite calcined much more cleanly at low temperature as shown by TGA (Figure 4a,c). After calcination at 600 °C in an atmosphere of dry air, the color of the undoped forsterite was dark brown, whereas the chromium-doped forsterite was bright, light green. In the doped xerogel, almost all of the organic groups were removed below 450 °C. In the undoped forsterite, however, about 10 wt % (presumably residual organic groups) remained at that temperature, but decomposed at 530 °C leaving about 1 wt % of carbon, as determined by elemental analysis.

When moisture was present in the atmosphere during calcination, there was less residual carbon in both chromium-doped and undoped forsterite. After calcination

at 600 °C in humid air, the color of the undoped forsterite was nearly white, and the chromium-doped forsterite was bright, light green. No abrupt weight loss was observed at 530 °C (Figure 4b,d). The undoped forsterite heated at 1000 °C in dry air or oxygen had black particles mixed with a white powder; whereas, the one heated in humid air was white. The chromium-doped forsterite precursor showed the same calcination behavior whether moisture was present or not.

This calcination behavior suggests that hydrolysis, esterification, and condensation reactions were occurring in the xerogel.³⁸ In the doped forsterite, chromium probably acted as a catalyst for removal of residual organics; many transition-metal oxides, including Cr_2O_3 , are catalysts for combustion analysis of organic compounds.^{40,41} Thus, most of the methoxy ligands were oxidized in the absence of water. The high yield of forsterite and the absence of MgO in the fired product (see below) ruled out significant loss of silicon species during calcination.

Firing. Because it was added in solution, chromium ion readily incorporated into the reactive magnesium silicate sol. By retaining this homogeneity in the xerogel, the diffusion barrier was minimized, and the precursor rapidly crystallized at low temperature. The doped forsterite started to crystallize at 600 °C and was fully crystalline at 800 °C within a few hours, as determined by powder XRD and FTIR spectroscopy. In situ high-temperature dynamic X-ray diffraction measurements (300 °C/h) showed that the precursor that was calcined in humid air started to crystallize at 560 °C and became fully crystalline at 800 °C.⁴² Earlier work had demonstrated that sol-gel prepared forsterite crystallized at ~ 850 °C,²¹ a temperature that is several hundred degrees lower than that required to prepare forsterite by solid-state ceramic techniques, in which repeated grinding and heating were required to achieve complete reaction.^{8,43-45} Since grinding introduces impurities, which may have a deleterious effect on the performance of forsterite as a laser material, the preparation of chromium-doped forsterite from pure components in solution was particularly advantageous.

Although SEM showed that the morphology of the xerogel was retained on firing at 1000 °C, the crystallite size, calculated by the Scherrer equation, was 85 nm. XRD patterns of such samples were taken to assess how much chromium could be introduced without formation of minor phases. Figure 5 shows representative XRD patterns of the polycrystalline chromium-doped forsterite for chromium to silicon mol ratios of 0.02 and 0.07. Below a mol ratio of 0.04, only forsterite was observed. Above 0.04, minor amounts of magnesiochromite (MgCr_2O_4) were observed, consistent with the phase diagram of $\text{MgO-SiO}_2\text{-Cr}_2\text{O}_3$.⁴⁶

IR spectra of polycrystalline chromium-doped forsterite powders having chromium to silicon mole ratios of 0.01

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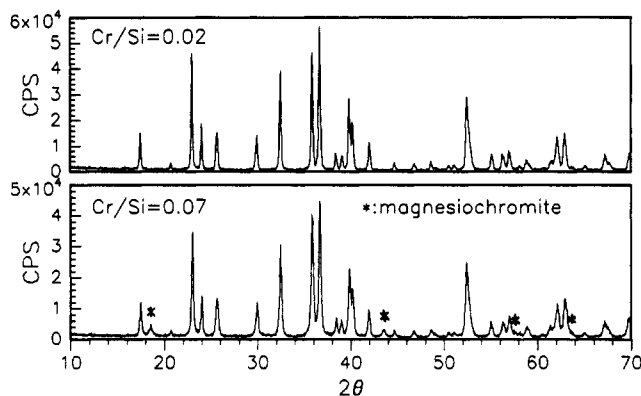


Figure 5. XRD patterns of polycrystalline chromium-doped forsterite.

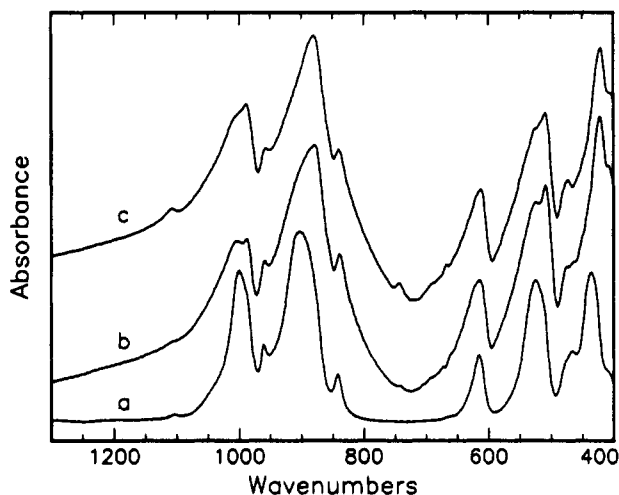


Figure 6. IR spectra of: (a) forsterite; (b) doped forsterite (Cr/Si mol ratio = 0.01); (c) doped forsterite (Cr/Si mol ratio = 0.02).

and 0.02 were compared to the spectrum of undoped forsterite (Figure 6). Undoped forsterite showed peaks at 1001, 961.5, 900.5, and 842 cm^{-1} (SiO_4 stretching), at 616.5, 522.5, 509 (sh) and 482 (sh) cm^{-1} (SiO_4 bending), and at 466.5 and 436 cm^{-1} for modes of octahedral MgO_6 ; this spectrum is essentially identical to that previously reported for forsterite.^{47,48} Upon doping with chromium, several new peaks developed. The following satellite peaks were observed next to major peaks the positions of which are enclosed in parentheses: 988.1 (1001), 879.7 (900.5, sh), 508.5 (522.5), 473.7 (466.5, sh), and 420.3 (436, sh) cm^{-1} . In addition, an extra peak, at 742.5 cm^{-1} , developed in the intermediate region of 800–650 cm^{-1} where there are no reported absorptions for SiO_4 or MgO_6 .^{47,48} The intensity of this peak, relative to those of Si–O stretching modes, was proportional to the chromium to silicon mol ratio. Several chromate compounds, such as $\text{Ba}_3(\text{CrO}_4)_2$, $\text{Sr}_3(\text{CrO}_4)_2$, or $\text{Ca}_3(\text{CrO}_4)_2$, which have discrete tetrahedral CrO_4 units, have a ν_1 peak near 770 cm^{-1} .⁴⁹ Replacing silicon and magnesium with their isotopes, ^{26}Mg and ^{30}Si , showed slight peak shifts especially for the nonsymmetric stretching modes, and the peaks at 842 and 615 cm^{-1} were insensitive to the replacement.⁴⁸ The same trend of peak shifts was observed for a series of olivines in which a large fraction of magnesium was replaced by several transition metal ions.^{47,50} On the basis of these observations, the

extra peak at 742.5 cm^{-1} is tentatively assigned to the Cr–O stretching vibration (ν_1). The satellite peaks are other Cr–O vibrational modes brought about by replacement of silicon and magnesium by chromium. That satellite peaks were observed for both Si–O and Mg–O vibrational regions is consistent with the replacement of chromium for both silicon and magnesium.

Single-Crystal Growth. In a preliminary study, samples containing large grains of chromium-doped forsterite were grown in an oxygen atmosphere by the floating zone methods, using fine-grained, polycrystalline chromium-doped forsterite as feedstock. The initial samples were hollow and had a diameter of 8–10 mm and a wall thickness of 2–4 mm. Very recently, large solid single crystals have been grown.⁵¹ The grains appeared blue when viewed down the crystallographic a axis and purple when viewed through the other axes. These colors may be compared to those (green and blue, respectively) seen in commercially available crystals grown in a more reducing atmosphere.

For comparison, the growth of crystals from mixtures of oxides was attempted. Although the mixture of metal oxides was ground and sintered several times prior to melting at ca. 1900 $^{\circ}\text{C}$, these attempts have not been successful on account of incomplete reaction during the short time of melting. Minor phases of cristobalite (SiO_2), enstatite (MgSiO_3), periclase (MgO), and magnesiochromite (MgCr_2O_4) together with forsterite were apparent by powder XRD. The formation of these minor phases is consistent with the phase diagram of MgO – SiO_2 , which shows enstatite, MgSiO_3 , to melt incongruently and decompose to forsterite and cristobalite upon cooling,⁵² and with the observation that the major product from the reaction of MgO and SiO_2 powders above 1500 $^{\circ}\text{C}$ was enstatite.⁴⁵

Characterization. As noted above, only a small amount of chromium dissolves in forsterite. Analysis of a typical fired powder, the precursor for which contained 0.37% Cr (by synthesis from CrO_3), showed $0.37 \pm 0.005\%$ Cr. Microprobe analysis of the single-crystalline grains indicated that magnesium was slightly in excess of the exact stoichiometry, as has been observed for crystals grown by the Czochralski method.¹² This analysis also showed that almost 90% of the chromium present in the precursor was lost during the single crystal growth; the mol ratio (Mg:Si:Cr:O) was 2.018/0.9904/0.0008/4 and 2.019/0.9995/0.0014/4 when the chromium to silicon mole ratio of the xerogel was 0.01 and 0.02, respectively. The extensive loss of chromium, caused by the high volatility of CrO_2 , required a relatively high rate of translation of the feed rod. This limitation was also the cause of the incomplete reaction when a mixture of oxides was used. The spatial distribution of Cr in the crystals is under investigation.

The single-crystalline grains were analyzed by ESR spectroscopy to identify dopant ions and to characterize the site occupation. Figure 7 is a representative ESR spectrum showing strong, sharp peaks for Cr^{3+} and a broad peak near zero-field energy, 450 G. No other resonances were observed except those due to very small amounts of

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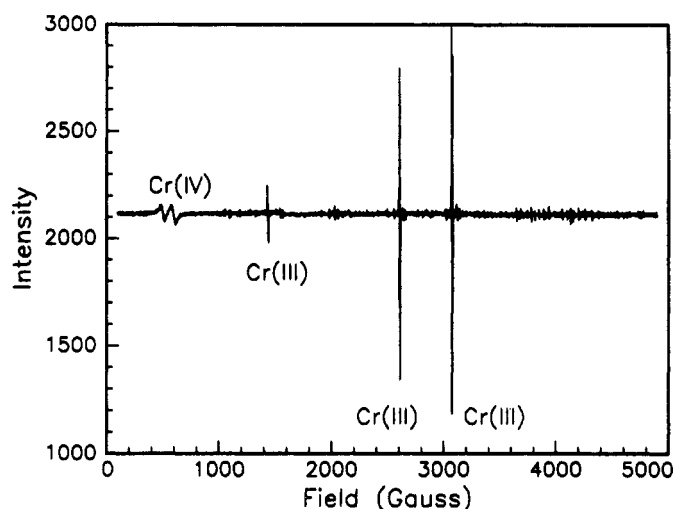


Figure 7. ESR spectrum of a chromium-doped forsterite single crystal. The b axis was parallel to the applied magnetic field. Splitting of the broad peak for Cr^{4+} into two peaks (at 500 G) was caused by misorientation of the crystal.

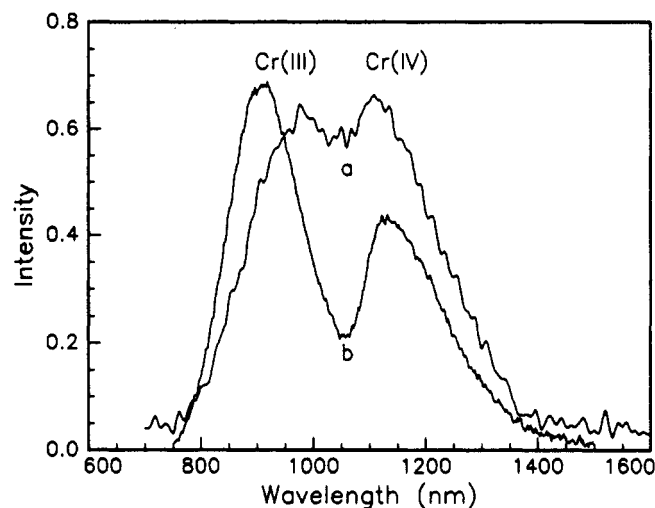


Figure 8. Emission spectra of chromium-doped forsterite single crystals: (a) grown in an oxygen atmosphere (see text); (b) commercial crystal grown by the Czochralski method.

manganese, a known impurity in the magnesium. The angular dependence of each chromium resonance, which is a very sensitive index of symmetrically nonequivalent sites, was analyzed. The angular dependence of the broad peak was consistent with a recent study done by Garrett et al.,⁵³ and the peak was assigned to Cr^{4+} in a tetrahedral site. The angular dependencies of the sharp peaks were identical to those reported as Cr^{3+} in octahedral sites of forsterite.⁵⁴ The intensity of the resonance for Cr^{4+} indicated that the ratio of Cr^{4+} to Cr^{3+} is high. The peak was not observed in previous studies for which the crystals were grown under a reducing atmosphere by the Czochralski method, probably because the $\text{Cr}^{4+}/\text{Cr}^{3+}$ ratio was too low.⁵⁴

Spectroscopic studies in the near IR region corroborated the high $\text{Cr}^{4+}/\text{Cr}^{3+}$ ratio implied by the ESR spectroscopic analysis. The UV-vis absorption spectrum, taken from a single crystal, was similar to that reported previously⁵⁵

and showed no peak for $\text{Cr}(\text{VI})$. The emission spectrum taken from a crystal that contained 0.01 mol % chromium (Figure 8a) and excited with 514.5-nm radiation exhibited a broad fluorescence band centered at 900 nm due to Cr^{3+} and an equally intense band near 1100 nm caused by Cr^{4+} .⁵⁶ In the spectrum of a commercially available crystal (Figure 8b), grown by the Czochralski method, the peak from Cr^{3+} was significantly more intense than that from Cr^{4+} .

The partial pressure of oxygen may not be the only factor controlling the oxidation state of chromium. Forsterite crystals doped with unspecified amounts of chromium and aluminum and grown under pure oxygen by the laser pedestal method, showed very little emission by Cr^{3+} .¹⁵ An ESR study of forsterite doped with chromium and aluminum indicated that there was an interaction between Cr^{3+} in the M2 octahedral site and Al^{3+} in a tetrahedral site, which could be a possible quenching route for the Cr^{3+} emission.⁵⁷ Such quenching may account for the absence of the band from Cr^{3+} in the doubly doped material.⁵⁷

Summary and Conclusions

By modification of the H_2O_2 -assisted sol-gel synthesis of forsterite,²¹ chromium was homogeneously doped into the magnesium silicate network. The methodology is being extended to several other transition metals. The sols are quite stable and have been used to spin-cast films of chromium-doped forsterite on various substrates.⁵⁸

For both chromium-doped and undoped forsterite, the cleanest calcination was achieved by pyrolyzing the xerogel in a stream of humid air. The xerogel readily turned to single phase, polycrystalline forsterite below 800 °C. This low processing temperature enhances processing of this material for several purposes, especially for the preparation of single-phase polycrystalline powder for a variety of uses (e.g., as feed rods for the LHPG production of fibers) and for the fabrication of crystalline films.

By employing fine-grained, chromium-doped forsterite as a feed stock, sintered rods were converted to polycrystalline samples having large single-crystalline grains in an atmosphere of pure oxygen. Emission of Cr^{4+} was significantly enhanced over that of a commercially available crystal. Preparation of pure single crystals of forsterite, doped with exclusively one or several metal ions, should now be possible by meticulously controlling the impurity levels in the sol-gel synthesis of precursors.

Acknowledgment. This work was supported by the MRL Program of NSF under Award No. DMR-9121654. We thank Dr. H. K. Kim and Prof. C. K. Ober for help with TGA measurements and Dr. D. E. Budil for helpful discussions on ESR spectroscopy.

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