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Toward Oxidatively Stable Interfaces in Fiber-Reinforced Ceramic Composites: Sol–Gel Synthesis of Potassium Fluorophlogopite

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Potassium fluorophlogopite, KFP, was synthesized by combination of a fluoridated magnesium silicate sol and an acetylacetone-modified potassium alkoxyaluminate complex. The best results were obtained when the sol was prepared by a multicycle process in which H_2O_2-assisted hydrolysis and condensation of tetramethylorthosilicate (generated *in situ* from tetraethylorthosilicate) alternated with fluoridation by aqueous HF. ^{29}Si NMR analyses of calcined gel precursors that were fired to 950 °C under dry air showed that the finely crystalline product, KFP contained minor amounts of a Q^0 species. To simulate the confined environment of an interface, between a fiber and a ceramic matrix, thin films were calcined then hot-pressed at 950 °C under Ar between two single-crystalline spinel substrates. X-ray diffraction analysis of the films showed KFP growth in a preferred orientation. Thin film growth was also observed between alumina substrates only when a forsterite barrier film was present between the KFP precursor and the substrate.

Introduction

High fracture toughness in fiber-reinforced composite materials requires strain tolerance to fracture as well as fiber pull-out at rupture. Thus, the interface between the fiber and the matrix should be strong enough to allow transfer of stress from the matrix to the relatively stronger fiber and yet weak enough to allow the fiber to pull out and deflect cracks in the matrix.[1–3]

Some glass ceramics that were reinforced with SiC fibers have shown high fracture toughness. This desirable property has been associated with the formation of a carbon-rich layer between the fibers and the matrix during processing.[4] However, considerable degradation of mechanical properties is observed after exposure of such a composite to air at 900 °C even for short periods of time.[5] This high-temperature embrittlement results from the oxidation and loss of the carbon-rich interface, most likely as CO.

Fiber coatings made from layered silicates that are oxidatively stable provide an alternative to the carbon interface.[6] The basic structural unit of the silicate framework is the SiO_4 tetrahedron. Tetrahedra may link together linearly by sharing one or two oxygens to form chains. The two-dimensional layers observed in phyllosilicates consist of chains linked together with the tetrahedra sharing three oxygens.[7] The use of fluoridated sheet silicates (i.e., F substituted for OH) would be especially advantageous as they have relatively high decomposition temperatures. A prime candidate for this purpose is synthetic potassium fluorophlogopite, $KMg_3(Si_3AlO_{10})F_2$ (KFP). Lacking hydroxyl groups in its structure, KFP can be used near 1200 °C,[8] whereas phlogopite, $KMg_3(Si_3AlO_{10})(OH)_2$, decomposes when heated above 1000 °C.[8]

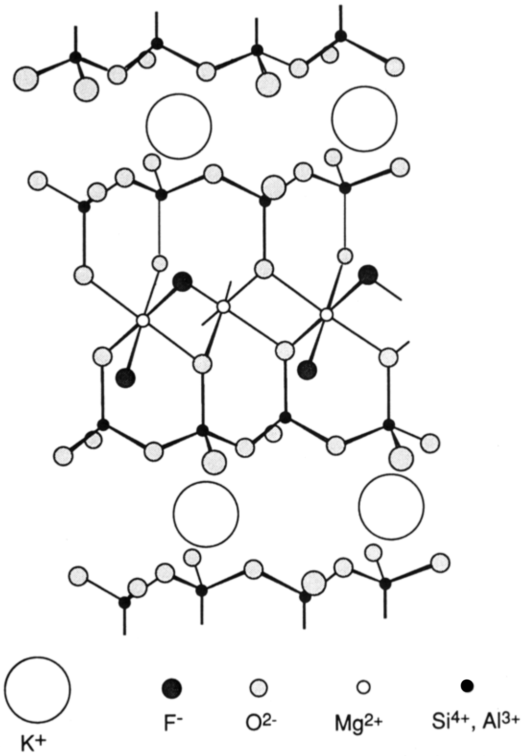

Figure 1. Crystal structure of potassium fluorophlogopite.

The crystal structure of KFP (Figure 1) has an octahedral layer between two tetrahedral layers (2:1 structure). The sheets are bonded together somewhat weakly by large,

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positively charged potassium ions to compensate for the net negative charge on the three layers.[9]

KFP has been previously synthesized from a variety of silicates, oxides, fluorides, hydroxides, and carbonates by one of three methods: internal resistance electric melting, arc resistance electric melting, and solid-state reaction.[10] Although single crystals can be produced from the above methods, products from these techniques cannot be used to coat fibers (typically 10–30 μm in diameter) or form thin films on various substrates. Sol-gel methods, however, have been widely applied to the preparation of films and coatings.[11]

This paper describes the sol–gel synthesis and characterization of powders and thin films of KFP by an extension of the peroxide-assisted synthesis of magnesium silicates recently developed in our laboratory,[12,13] augmented by fluoridation. Some results involving powders have been communicated previously.[14]

Experimental Section

General Comments. All precursor synthesis operations were carried out under a dry argon atmosphere unless otherwise noted.[15] Reagent grade methanol was twice distilled from magnesium methoxide. 2-Methoxyethanol was dried over sodium metal, degassed, and distilled. TEOS (99+%), $Al(OBu^s)_3$, potassium metal, hydrogen peroxide (30%) and 2,4-pentanedione were obtained from Aldrich Chemical Co. Magnesium chips (99.99%) were obtained from Alfa Chemicals. Aqueous HF (analyzed to be 48.8%) was obtained from Mallinckrodt. Randomly oriented single crystalline spinel and sapphire substrates were obtained from Meller Optics. The National Nanofabrication Laboratory at Cornell University provided the SiO_2-coated silicon (001) wafers.

A Mattson FTIR GL-4020 spectrometer was used to record spectra of powders. XRD patterns for powders and thin films were recorded using a Scintag PAD V diffractometer. Some ^{29}Si MAS NMR spectra were obtained using a Bruker AF300 spectrometer with a DOTY MAS probe; samples were packed in a sapphire rotor with Vespel end caps. A Chemagnetics CMX-300 spectrometer was used to record ^{19}F and ^{29}Si MAS NMR spectra using a pencil type rotor with a zirconia sleeve. Microprobe analyses were done using a JEOL Superprobe 733, Tracor Northern 5500. Sputtering ESCA analyses were done at Corning, Inc. using a Phi 5500 XPS/scanning Auger microprobe. XRD powder patterns were calculated using the program LAZY PULVERIX.[16] A characterized sample of KFP, synthesized from the melt, was provided by Dr. Kenneth Chyung, Corning, Inc.

Potassium Acetylacetonato Alkoxy Aluminate (KAAAl) Solution. In a nitrogen-filled drybox, 0.7314 g (0.018 71 mol) of potassium metal and 4.606 g (0.018 70 mol) of $Al(OBu^s)_3$ were weighed into separate flasks. Working on a double manifold inert atmosphere system, 2-methoxyethanol (~20 mL) was added by syringe to the potassium; gas and heat evolution were observed. Similarly, the aluminum alkoxide was dissolved in ~20 mL of 2-methoxyethanol delivered using a syringe. Both the potassium and aluminum alkoxide solutions were transferred quantitatively via a cannula into a 100-mL volumetric flask that was modified with a sidearm stopcock for gas inlet. The resulting solution was diluted to volume with 2-methoxyethanol.

KFP Sol (Methods A and B). A 500-mL Schlenk reaction vessel (SRV) containing about 250 mL of freshly distilled MeOH and a magnetic stir bar was charged with Mg chips (0.5290 g, 0.021 76 mol). The SRV was placed in an ice bath and was equipped with a water-cooled condenser and three-way gas adapter. The mixture was stirred under a very slow flow of Ar. Vigorous gas evolution was observed until all the Mg reacted. The colorless, nearly clear $Mg(OMe)_2$ solution was quantitatively filtered (D-porosity frit) into a 250-mL addition funnel.

By quantitative cannula transfer, TEOS (4.516 g, 0.021 70 mol), was added with stirring to the $Mg(OMe)_2$ solution to obtain a clear, colorless solution. The addition funnel that contained the solution of alkoxides was attached to a creased 1-L, three-necked flask (Morton type, Ace Glass Co.) charged with 100 mL of MeOH. The flask had been equipped with a mechanical stirrer and a Y-shaped adapter that was fitted with a septum and a water-cooled condenser with a three-way gas adapter.

Hydrogen peroxide (1.16 g, 0.0102 mol of H_2O_2) was withdrawn into a 60-mL plastic syringe containing MeOH (50 mL). The syringe needle was attached to a cannula using a thin polyethylene tube, and the cannula was inserted into the reaction vessel through the septum. Similarly, 0.6320 g of 48.8% aqueous HF (0.015 42 mol) was withdrawn through a polyethylene needle into a 60-mL plastic syringe containing MeOH (50 mL). The needle was inserted into the septum by means of a short, larger gauge steel needle passed through beforehand. Then the steel needle was withdrawn.

In method B, a portion (10% by volume) of the alkoxide solution was added, with vigorous stirring, to the MeOH in the reaction flask. While continuously stirring the reaction mixture, ~10% of the H_2O_2 solution was added, using a syringe pump, at 0.67 mL/min, followed by 10% of the HF solution, added at the same rate. The alternating addition of 10% portions was repeated until all the reactants had been consumed. A very slightly hazy sol with a bluish tinge was obtained.

For method A, the alkoxide solution was transferred to the reaction flask that had been charged with ~100 mL of MeOH. While being stirred, the alkoxide solution was hydrolyzed by addition of all of the H_2O_2 solution, using a syringe pump, at 0.67 mL/min. This was followed by the addition of all of the methanolic solution of HF at 0.67 mL/min. The sol obtained was slightly hazy.

For both methods A and B, a pale yellow solution of 0.74 mL of 2,4-pentanedione (7.7×10^{-3} mol) and 38.7 mL of KAAAl solution (7.7×10^{-3} mol) was added dropwise, with stirring, to the magnesium fluorosilicate sol.

KFP Sol (Method C). A solution of magnesium methoxide prepared from 0.5320 g of Mg (0.021 89 mol) and TEOS (4.544 g, 0.021 84 mol) was prepared as described above. A pale yellow solution of 38.4 mL of KAAAl (7.3×10^{-3} mol) and 0.75 mL of 2,4-pentanedione (7.3×10^{-3} mol) was added to the clear, colorless magnesium silicate solution in a 250-mL addition funnel. The resulting hazy white solution became more cloudy upon standing, although no precipitate was observed. The addition funnel that contained the mixture of alkoxides was attached to a 1-L three-necked creased flask containing 100 mL of MeOH and equipped similarly to the reaction vessel used for method B.

The alkoxide solution was hydrolyzed by addition of 1.168 g (0.010 30 mol) of 30% H_2O_2 (in 50 mL of MeOH) and was fluoridated with aqueous HF (0.5960 g, 0.014 54 mol) in 50 mL of MeOH using the ten-portion cycle addition similar to method B. The sol obtained was very slightly hazy.

Preparation of KFP Precursor Powders. Working in the air, the sol was transferred into a 1-L round-bottom flask and was concentrated with a rotary evaporator at reduced pressure. To reduce drying time, the thin, slightly yellow slurry so obtained was dried with a heat lamp (250 W at ~30 cm from the surface of the slurry) in a 1-L polyethylene beaker that was loosely covered with a watch glass. To reduce residual carbon, the resulting yellow xerogel was ground into a powder with a mortar and pestle, then was moistened with a few milliliters of 30% H_2O_2, and dried under a heat lamp for several hours. The resulting white powder was placed in alumina boats and was calcined at 600 °C for 6 h in a flowing atmosphere of dry air in a *tube* furnace. Using XRD, the formation of KFP was monitored at different stages of firing (700, 800, 900, 950, and 1100 °C) under the same conditions.

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Preparation of KFP Thin Films. Substrates were cleaned in an ultrasonic bath for 5 min each in dilute ethanolic HCl, 95% EtOH and distilled, deionized H_2O. A portion of the sol, prepared from method B, was placed in an ultrasonic bath for 5 min and was drawn into a syringe then passed through a 0.45-μm PTFE filter. The substrate was covered with the filtered sol, and was spun at ~2500 rpm for 40 s. The coated substrate was air dried for about a minute before application of the next coat. The resulting film was dried in an oven at 112 °C for 2 h after every third coat. Eighteen to twenty-one coats were placed on the substrate. The coated substrates were heated to 300 °C at 25 °C/h and held for 9–12 h under a flow of dry O_2. The films were then covered with uncoated substrates and were hot-pressed for 1 h between carbon rods in an Ar atmosphere in a furnace at 950 °C; the ramp rate was 200 °C/h and the load was either 90 or 900 kg.

To prepare KFP films that had a barrier layer of forsterite, five layers of filtered forsterite precursor sol[12] were spin-coated onto a clean sapphire substrate at approximately 2500 rpm for 40 s. The forsterite-coated substrates were then calcined at 400 °C or calcined and fired at 1000 °C in a box furnace. Filtered KFP sol was then spin-coated onto the precoated substrates using the procedure outlined above. A forsterite-coated substrate was used to cover the calcined KFP film. The "sandwiched" film was hot-pressed in an Ar atmosphere at 950 °C for 1 h with a 900-kg load.

Results and Discussion

Most protocols for the sol–gel synthesis of multicomponent products are designed to achieve homogeneous mixing of components by combining all of them in solution, allowing the mixture to gel, and then calcining the xerogel to obtain a powder that's subsequently fired to form a ceramic.[11] By combining the ingredients in a logical, sequential fashion, however, we may be able to lower the activation barrier to form a particular structure type, guided by the product's known or expected structural features. Thus, the strategy is to form in the xerogel as many of the chemical bonds needed in the product as possible and avoid forming ones that will have to be broken, especially if they are very stable. Since KFP contains Mg–F bonds in place of the Mg–OH bonds in the octahedral (central) region of the sheet (Figure 1),[17] the formation of Mg–F bonds early in the process was designed to facilitate the formation of the desired structure.

The synthetic scheme for KFP (Figure 2) was based on methods previously used for simpler magnesium silicates.[12,13] The slow addition of a methanolic solution of 30% H_2O_2 alternated with the addition of 48% HF to the starting alkoxides in a multistep preparation of the magnesium silicate fluoride sol (Method B in Figure 2). The use of H_2O_2 facilitated the hydrolysis and condensation of $Mg(OMe)_2$ and TEOS, which would otherwise react at very different rates, thereby precipitating $Mg(OH)_2$.[12,13] The magnesium silicate fluoride sol was then combined with a potassium acetylacetonato alkoxyaluminate precursor (KAAAl) to give the sol from which the product, KFP-B was obtained. In method A, instead of a multistep process, HF was added to the alkoxide mixture after all of the hydrogen peroxide had been added.

Compared to sequential mixing of precursor solutions (method A in Figure 2), the repetitive addition of the hydrolysis agent, H_2O_2, followed by the fluoridating agent, HF, gave the desired product more efficiently (see discussion of XRD below). For method A, the fluoridating agent may not effectively penetrate the magnesium silicate network that forms during the simultaneous hydrolysis and condensation that occurs.

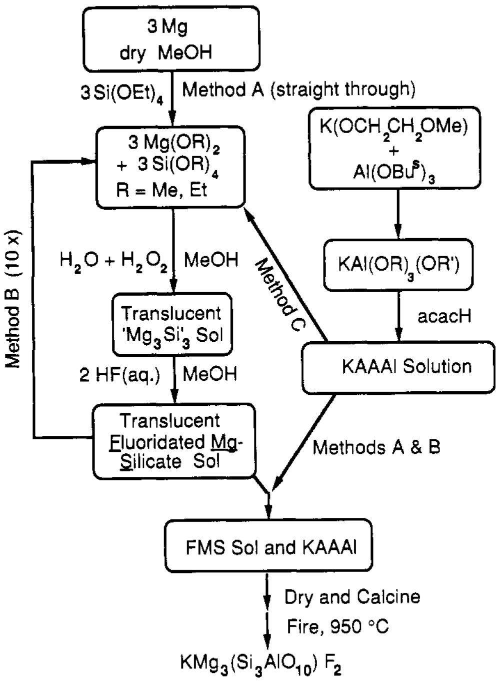

Figure 2. Scheme for synthesis of KFP by sequential mixing of component solutions (method A) and multistep, portionwise additions (methods B and C).

Analysis of the headspace above the unhydrolyzed magnesium silicate solution by gas chromatography showed the *in situ* production of tetramethylorthosilicate (TMOS) from TEOS by transesterification.[18] This exchange, caused by magnesium methoxide, was previously observed in the synthesis of forsterite. The presence of small amounts of $Mg(OMe)_2$ generated *in situ* a magnesium-containing catalyst that caused condensation of the products of the hydrolysis of TMOS by methanolic H_2O_2.[18,19] Enough 30% H_2O_2 was added to the sol to hydrolyze one-half of the alkoxide groups on magnesium and silicon. The extent of hydrolysis of TMOS was monitored by GC analysis of the headspace above the sol.[18] Headspace analysis showed that after all the H_2O_2 and HF solutions had been added, approximately 25% of the TMOS remained unreacted.

The preferential formation of Mg–F bonds[20,21] to the more stable Al–F bonds[22,23] was promoted by the protocol adopted for combining starting materials, i.e., the aluminum-containing component was not brought into contact with the fluoride-containing components until the final step of sol preparation. To further safeguard against reaction with HF, potassium alkoxyaluminate was modified with a chelating agent, 2,4-pentanedione (acacH). This complexation also prevented the precipitation of aluminum methoxides that are insoluble in the solvent, methanol. Since $Al(OBu^s)_3$ has been reported to react with the enol form of acacH by substituting for a *sec*-butoxide group in an acid–base reaction,[24,25] it is likely

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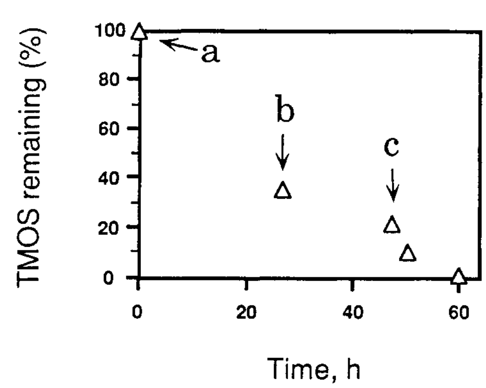

Figure 3. Unreacted TMOS during the synthesis of KFP by method B: (a) before hydrolysis and fluoridation; (b) at the end of addition of H_2O_2 and HF; and (c) start of addition of KAAAl.

that a similar reaction would occur with the more basic aluminate complex, $K[Al(OR)_3(OR')]$ ($R = Bu^s$, $R' = CH_2CH_2OCH_3$); the enolic content of acacH is about 76.4%.[26]

GC analysis of the headspace over the sol[18] showed that addition of KAAAl to the magnesium silicate sol drives the hydrolysis reaction of TMOS to completion, probably aided by the presence of a potassium base acting as a catalyst. The rapid decrease in the concentration of TMOS after the addition of the KAAAl solution is evident in Figure 3.

To test the efficacy of the above protocol, i.e., addition of the chelated aluminum alkoxide after magnesium had been fluoridated, a variation to the procedure (method C in Figure 2) was tried. This route involved adding the KAAAl precursor directly to the solution of magnesium and silicon alkoxides. The resulting mixture was combined in portions alternately with H_2O_2 and HF solutions in methanol. Although preliminary observations suggested that a greater amount of amorphous material and less crystalline KFP were obtained for method C,[14] subsequent syntheses did not show any significant difference in product crystallinity and composition. It appears, therefore, that the chelation of aluminum and the probable sequestering of some of the Mg–F bonds in the silicate network minimizes the formation of amorphous components on firing.

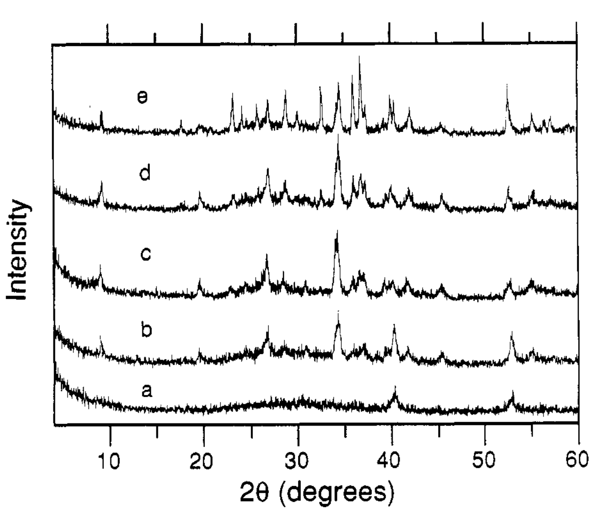

Figure 4. XRD powder patterns of H_2O_2-treated xerogels (from method B, see text): (a) calcined at 600 °C, and fired at (b) 800, (c) 900, (d) 950, and (e) 1100 °C.

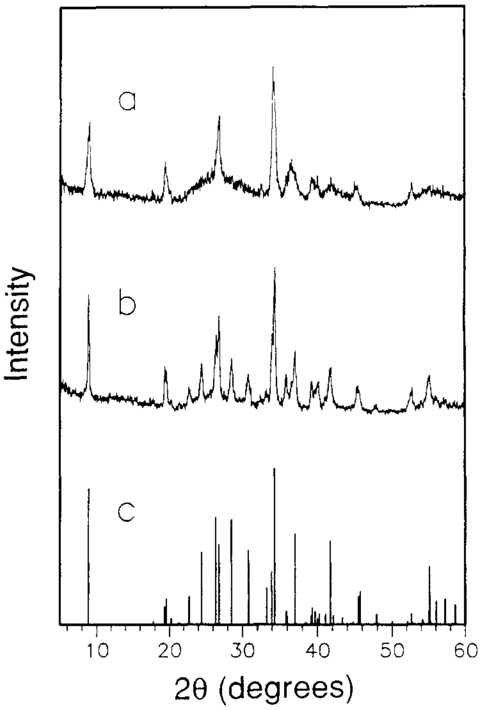

Figure 5. Comparison of powder XRD patterns of precursors to KFP from (a) method A and (b) method B, after being fired at 950 °C, with the calculated pattern (c).

XRD analysis of the xerogels from Method B calcined at 600 °C (Figure 4) shows mainly an amorphous or glassy phase, as suggested by the broad diffraction feature around 30° (2θ). Broad peaks around 40 and 53° (2θ) were also observed. Precursor powders fired at 800, 900, 950, and 1100 °C gave diffraction patterns that indicated the formation of a layer structure by the appearance of a peak at ~9° (2θ). At 950 °C, KFP was the principal phase; the peak positions and peak intensities closely match the diffraction pattern calculated for KFP (Figure 5b,c). The observed intensities do not match patterns in the literature, probably due to preferred orientation usually observed in natural KFP and KFP synthesized by solid-state techniques.[27] At 1100 °C, peaks at ~22.9, 32.3, 35.7, and 36.5° (2θ), assigned to forsterite were observed.[28] Forsterite is a known byproduct in the decomposition of KFP by loss of fluoride through reaction with water in the air; other reported byproducts, leucite, and glass, were not observed by the XRD analysis.[10]

Increased homogeneity in the sol leads to less segregation in the gel and glass, thereby producing better crystallized KFP as the major product after firing. This improvement can be seen from the narrower peak widths of the X-ray diffraction pattern of KFP prepared by the step-wise addition (Figure 5a,b).

Although the XRD patterns of the fired xerogels suggest that amorphous intermediates convert directly to KFP, ^{29}Si MAS NMR spectra showed short-range order in local bonding environments. The ^{29}Si NMR spectrum of the dried xerogel (Figure 6a) showed the presence of three local environments around silicon with overlapping peaks

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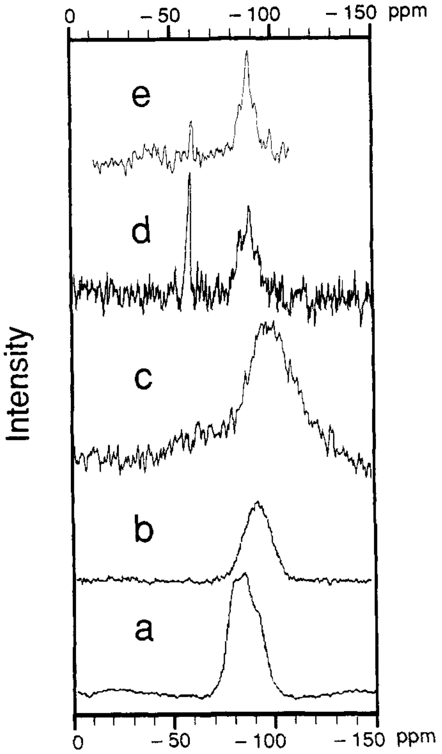

Figure 6. ^{29}Si MAS NMR spectra of KFP precursors (method B): (a) uncalcined xerogel and after H_2O_2 treatment (b), calcination at 600 °C (c), and firing at 800 °C (d) and 950 °C (e).

at −80.6, −85.9, and −93 ppm, centered at ∼−86 ppm. The shifts are within the range for aluminosilicates with Q^3(nAl) silicon environments, where n = 0, 1, or 2.[29] The ^{29}Si NMR spectrum of the dried powder treated with H_2O_2 prior to calcination showed further condensation (Figure 6b); the broad peak shifted to higher field and was centered at ∼−92 ppm. The spectroscopic dispersion (i.e., the number of Si environments), as judged by the width of the peak, appears to be large and does not eliminate the presence of Q^4 species (i.e., Si bonded to four OSi groups), since the baseline upfield of −100 ppm is nonzero. The xerogel calcined at 600 °C gave a broad NMR signal centered at ∼−95 ppm (Figure 6c). The main peak appears to overlap with a broad signal at ∼−60 ppm. After firing at 800 °C, the precursor powder showed a peak at −61 ppm, and a set of overlapping peaks at −85, −89, and −92 ppm were observed. We assign the latter three peaks to Q^3(2Al), Q^3(1Al), and Q^3(0Al) respectively, in KFP; the reported spectrum gave peaks at −85.2, −89.2, and −92.7 ppm.[30] The peak at −61 ppm is assigned to (SiO_4) or Q^0 species. We had tentatively assigned this Q^0 peak to forsterite,[29] but since the XRD pattern does not show any forsterite at 800 °C, that assignment must be reconsidered.

The formation of a humite mineral ($n Mg_2SiO_4 \cdot Mg(OH,F)_2$, n = 1–4) was inferred from the TGA of a glass of KFP composition that showed an exotherm at ∼650 °C.[10] Chen assigned this exotherm to a pseudocrystalline intermediate that may have a sheet structure.[31] Chondrodite is a fluoridated nesosilicate (Si in Q^0 environment) with a ^{29}Si NMR shift at −60 ppm.[32] Thus, a better assignment for the peak at −61 ppm in the KFP precursor would be a humite mineral, chondrodite or norbergite. In support of this assignment, the XRD pattern of the KFP precursor calcined at 800 °C showed broad peaks at 40, 53, and 63° (2θ) which correspond to several major peaks of these humite minerals.[33,34]

The ^{29}Si NMR spectrum of the precursor fired at 950 °C contained peaks at −85.4, −89.7, and −92.9 ppm, which closely correspond to those of an authentic sample of melt-synthesized KFP (−85.3, −89.1, and −93.3 ppm). In addition, a peak at −61.9 ppm was also present. There was a noticeable increase in the total area of the peak at −61.9 ppm after the xerogel was fired to 1100 °C. Since peaks characteristic of forsterite were observed by XRD analysis of this sample, it is likely that the increase is caused by this decomposition product.

The ^{19}F MAS NMR spectrum of the dried, unfired xerogel, prepared using Method B, had a broad peak centered at −190.9 ppm relative to $CFCl_3$. The width of the peak suggests some dispersion in the types of fluoride environment in the glass, including some bonded to magnesium; the chemical shift for MgF_2 is −198.3 ppm.[35] The xerogel prepared according to Method B, treated with H_2O_2 and calcined at 600 °C showed a broad ^{19}F signal centered near −179 ppm with a shoulder at −186 ppm. After firing at 950 and at 1100 °C, the ^{19}F NMR spectra of the powders gave single peaks at −176.2 and −176.8 ppm, respectively. These shifts are in good agreement with the −175.9 ppm shift that was observed from an authentic sample of melt-synthesized KFP.

Other Aluminum Chelates. With the intent to minimize the formation of byproducts including forsterite, the effect of other aluminum chelates on the product composition was investigated. *trans*-1,2-Diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid (H_4CDTA) and ethylene glycol were substituted for acacH in the synthesis. Compared to acac$^-$, tetradentate CDTA^{4-} is expected to bind more strongly to aluminum. On the other hand, neutral ethylene glycol is a weaker chelate compared to acac$^-$.

The CDTA-complexed potassium alkoxyaluminate precursor was prepared by adding H_4CDTA to potassium 2-methoxyethoxide and then adding $Al(OBu^s)_3$ dissolved in 2-methoxyethanol to the stirred suspension. The clear, colorless solution was added to the fluoridated magnesium silicate sol. The gel obtained on removal of the solvent was treated with H_2O_2 before calcination and firing. Unlike the gels synthesized with acacH as chelating agent, the CDTA modified gels showed more carbon residue (see below), which persisted even after firing at 950 °C. XRD analysis showed that the product was not as crystalline (broader peaks) as acacH-chelated gels processed under similar conditions and that the CDTA modification did not inhibit forsterite formation.

Xerogels chelated with ethylene glycol were prepared using method B; the glycol was added directly to the

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potassium alkoxyaluminate solution. After treatment with 30% H_2O_2 and calcination at 300 °C for 12 h, the xerogel was white. XRD analysis of fired xerogels showed the presence of a minor amount of forsterite as well as crystallization behavior similar to that observed for acacH-chelated precursors.

Precalcination Processing. Moistening xerogels with 30% hydrogen peroxide before calcination and firing helped reduce residual carbon. The peroxide may act as combustion aid,[36] and the additional water it provides may promote hydrolysis and condensation reactions that facilitate the removal of organic ligands as alcohols. Without H_2O_2 treatment, products ranged from light gray (a mixture of white and black particles) to black. The presence of residual carbon has been attributed to the incomplete combustion of organics, particularly the chelates used in the syntheses.[37] However, treatment with H_2O_2 was not beneficial in the case of the more strongly bound chelate, CDTA. The powders obtained were gray to black even after firing at 950 °C. Furthermore, a question that arose was whether hydrogen peroxide precalcination treatment of KFP xerogels may be promoting forsterite formation. Work done on simpler magnesium silicate systems in our laboratory suggested that hydrogen peroxide pretreatment can cause segregation of Mg-rich phases in the fired product, e.g., formation of forsterite (Mg_2SiO_4) from an enstatite ($MgSiO_3$) xerogel.[38]

As an alternative to H_2O_2 pretreatment, the acacH-chelated precursor powders were treated with water[39] and dried thoroughly prior to calcination. H_2O-treated, calcined and fired powders were predominantly white with some black flecks compared to a totally black powder for an untreated xerogel processed similarly. The H_2O_2 treated precursor was white. However, comparison of XRD patterns for H_2O and H_2O_2 treatments showed no substantial difference at the different temperatures. The product from the H_2O_2 treated gel is probably somewhat better crystallized, based on the narrower width of the peaks in the XRD pattern. Both pretreatments also yielded forsterite as a minor phase when fired above 900 °C.

Thin Films. Preliminary efforts to prepare thin films of KFP on various substrates such as silicon, SiO_2-coated silicon, and sapphire were hampered by loss of fluoride during calcination and by the amount of residual carbon left on the film.[14] The sol was spin-coated onto the substrates, and the films were fired at 950 °C in a tube furnace in a stream of dry air for varying lengths of time (from 5 min to a few hours). According to glancing angle XRD analysis, amorphous films were obtained after firing. Forsterite was observed in some cases when sapphire was used as the substrate, suggesting loss of fluoride. Since the films were only a few hundered angstroms thick, even minute traces of water vapor could easily diffuse through the film thereby enhancing loss of fluoride, possibly as HF or as SiF_4. Loss of fluoride as KF, observed during the decomposition of KFP under vacuum, is also possible.[10] Fluoride content as low as 2 wt % has been analyzed on a film sample on sapphire (measured by sputtering ESCA) that was heated using the same heating schedule for powders; the stoichiometric composition of KFP has 9% F. Extended heating led to even larger fluoride losses. To reduce fluoride loss, films were fired for a much shorter time in a preheated tube furnace with dry air flow. This firing schedule (and possibly increased film thickness) improved fluoride retention to about 5 wt % in a film that was dip-coated on fused silica and heated at 950 °C for 2 min but increased the amount of residual carbon; the film obtained was gray to black and contained no KFP by XRD.

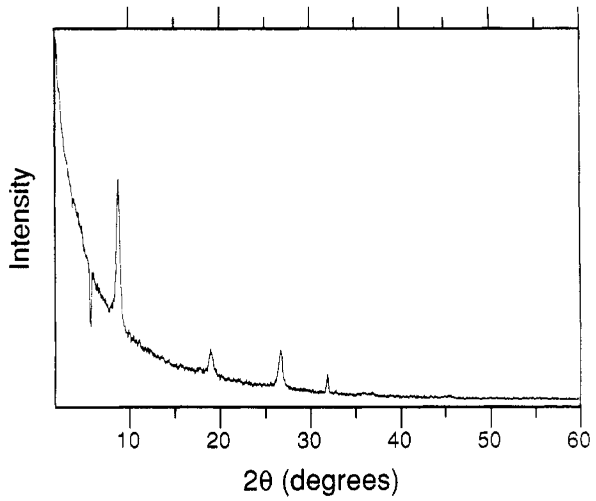

Figure 7. Glancing angle XRD pattern of KFP thin film between single crystalline spinel substrates, hot-pressed at 950 °C for 1 h at 90-kg load.

Another concern that had to be addressed was the reactivity of the film with the substrate. In studies involving KFP reaction couples, Cooper and co-workers reported that KFP reacts with alumina to form spinel ($MgAl_2O_4$).[40] KFP was also found to be reactive with mullite and enstatite but was stable against spinel, forsterite, and leucite. These results suggest that KFP films might form on spinel substrates or on alumina substrates protected by an unreactive barrier layer such as forsterite.

To address both problems and to simulate the conditions that the coating would undergo during the processing of a fiber-reinforced composite, spin-coated films were hot-pressed in a "sandwich" configuration. A total of at least 18 layers of a KFP sol were spin-coated on single crystalline spinel substrates; the film was calcined at 300 °C for 12 h. The calcined film was covered with another substrate and the combination was hot-pressed under argon flow. Glancing angle XRD analysis (Figure 7) showed that KFP formed within an hour at 950 °C under a load of 90 or 900 kg. Two of the peaks in the XRD pattern at ~9 and 27° (2θ) come at the expected positions for the (001) and (003) reflections of KFP.[9] The peaks at ~19.5 and 32° (2θ) are from the single-crystalline spinel substrate. Microprobe analysis (WDS) of the film gave a Si:F:K ratio of 3:1.7:1.1 (expected ratio is 3:2:1). The other half of the "sandwich" also appeared to have KFP on it. When the experiment was repeated, with a different spinel substrate, different ratios of intensities of the XRD peaks from KFP were observed. Such variations may be the result of preferred growth or orientation on the randomly oriented substrates.

KFP films on Si(100) wafers that were hot-pressed at 950 °C for 1 h under a 9-kg load so as not to crush the

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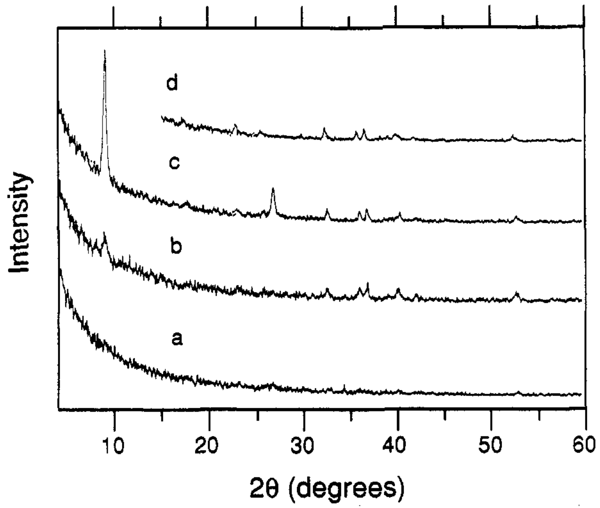

Figure 8. Glancing angle XRD patterns of KFP thin film hot-pressed for one hour at 950 °C, 900-kg load: (a) between single-crystal alumina, (b) with calcined forsterite barrier layer, (c) with crystalline forsterite barrier layer. (d) XRD pattern for the fired forsterite barrier layer prior to spin-coating of KFP sol.

substrate gave no signs of crystallinity by XRD glancing angle analysis.

To test the hypothesis that reactivity of the substrate with KFP or its precursor may occur during processing, KFP films "sandwiched" between single-crystalline sapphire substrates were hot-pressed under Ar at 950 °C for 1 h with a 900-kg load. Glancing angle XRD analysis (Figure 8a) indicated no mica formation, i.e., no peak near 9° (2θ). In contrast, if a forsterite precursor sol were spin-coated onto the alumina substrate and fired prior to the application of the KFP film, the mica layer formed as before (Figure 8b).[41] KFP also crystallized when the barrier layer was amorphous; the forsterite film was calcined at 400 °C, a temperature well below that required for its crystallization (Figure 8c).[12] XRD peaks from forsterite and KFP were observed in both cases. The reaction between forsterite and alumina to form cordierite, spinel and sapphirine has been reported to be kinetically unfavorable at room temperature. This may be the reason for the absence of any observed reaction between the forsterite barrier layer and the substrate.

Summary and Conclusions

The synthesis of potassium fluorophlogopite was best achieved from a precursor sol prepared by alternating, portionwise hydrolysis and fluoridation of a solution of magnesium and silicon alkoxides, followed by addition of a potassium alkoxyaluminate solution chelated with 2,4-pentanedione. Treatment of the xerogel with 30% H_2O_2 before calcination and firing was necessary for the complete removal of carbon-containing materials. On firing, conversion of the powder to KFP may proceed, at least partially through a humite intermediate, norbergite or chondrodite.

Crystalline KFP films were prepared by hot-pressing films of the precursor between unreactive substrates such as spinel. Such confinement limits loss of fluoride and closely approximates conditions used to prepare KFP-coated fiber-reinforced composites using a glass-ceramic matrix. Alternatively, a nonreactive barrier layer (e.g., forsterite) between the KFP precursor and the substrate limits the reaction of the film with the substrate. Film preparation has been extended to coating of fibers with the KFP sol, with or without a barrier layer, for the fabrication of fiber-reinforced, ceramic matrix composites. Details of these experiments will be reported elsewhere.

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