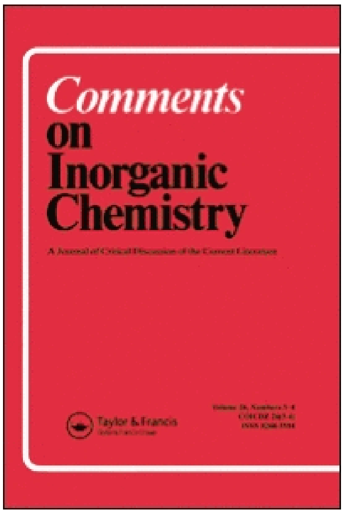

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Liquid Metal Carboxylates as Precursors for Aluminum-Containing Ceramics

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Liquids salts of aluminum, magnesium, and yttrium were prepared via the reaction of 2-[2-(2-methoxy)ethoxy]ethoxyacetic acid (MEEA) with aluminum basic acetate, magnesium hydroxide, or yttrium carbonate, respectively. These salts may be used to prepare liquid precursors for binary aluminum-containing ceramics by dissolution of metal nitrates in one of the liquid metal carboxylates. In this manner, preceramic liquids were synthesized that yielded magnesium, copper, and nickel spinels and yttrium aluminum garnet at temperatures as low as 600°C. The carboxylates may also be used to prepare spinel at 700°C by a modified powder process in which alumina is coated with magnesium oxide using $Mg(MEEA)_2$. In a similar approach, liquid aluminosilicate precursors were prepared by suspension of nano-particulate silica in $Al(MEEA)_2OH$.

Keywords: *spinel, garnet, aluminosilicate, carboxylate, ceramic precursor*

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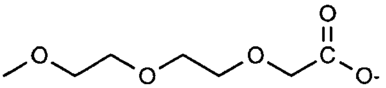
INTRODUCTION

The recent discovery of a family of metal carboxylates[1–4] that are liquids at room temperature has provided novel approaches for the preparation of refractory ceramic bodies and the synthesis of ceramic films by liquid phase processing.[5] These carboxylates, salts of 2-[2-(2-methoxy)ethoxy]ethoxyacetate, **1**, have polyether linkages which undoubtedly contribute to their unusual characteristics by chelating and "solvating" the metal ions.



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One technique for the use of these liquid precursors in the preparation of ceramic thin films is metallo-organic deposition MOD,[6,7] a non-vacuum, solution-based method of depositing thin films. In the MOD process, a suitable metallo-organic precursor dissolved in an appropriate solvent is coated on a substrate by spin-coating, screen printing, or spray- or dip-coating. The soft metallo-organic film is then pyrolyzed in air, oxygen, nitrogen or other suitable atmosphere to convert the precursors to their constituent elements, oxides, or other compounds. Shrinkage generally occurs only in the vertical dimension so conformal coverage of a substrate may be realized. Metal carboxylates with long slightly branched alkyl chains (e.g., 2-ethylhexanoate or neodecanoate) are often used as precursors for ceramic oxides since they are usually air stable, soluble in organic solvents, and decompose readily to the metal oxides. MOD processes for the generation of many oxide-based materials have already been developed: e.g., $BaTiO_3$,[8] indium tin oxide,[9] SnO_x,[10] $YBa_2Cu_3O_7$[11] and ZrO_2.[12]

The increasing demand for environmentally friendly processes places stringent requirements on precursors for ceramic materials. In particular, the avoidance of organic solvents necessitates the development of preceramic compounds that are either water soluble or which are amenable to solventless processing. Therefore, the metal salts of 2-[2-(2-methoxy)ethoxy]ethoxyacetate are very attractive MOD precursors since they are hydrolytically stable and are usually liquids. Furthermore, these liquids are excellent solvents for other metal salts so that precursor solutions for multi-metallic ceramic materials are readily prepared. Previously, a homogeneous precursor solution for nickel ferrite was synthesized by dissolution of $Ni(NO_3)_2$ in the liquid iron carboxylate, $Fe_3O(MEEA)_7 \cdot 5.5\ (H_2O)$.[4] This precursor solution yielded a metastable, amorphous $NiFe_2O_4$ phase at 300°C which underwent an exothermic crystallization at 374°C to yield the trevorite phase of $NiFe_2O_4$.[4] Barium titanate has also been synthesized using a liquid metal carboxylate precursor that was prepared by dissolving barium acetate in $Ti(MEEA)_4$.[3]

The application MOD processing in the preparation of integrated circuits or sensors requires patterning of the ceramic film. This is readily achieved at several different points in the MOD process: during the deposition step, after deposition and prior to pyrolysis, during pyrolysis or after pyrolysis. MOD films have been patterned during deposition by screen printing[13,14] and ink jet printing,[15] but a variety of other methods such as spraying through a stencil and off-set printing are also applicable.[8] Solutions of traditional MOD precursors often do not have sufficient viscosity for screen printing,[8] but the high viscosity of the liquid metal carboxylates makes them very suitable precursors for solventless screen printing. Another very useful method of patterning MOD films is performed during the pyrolysis step by use of a laser,[16,17] electron beam,[18] or an ion beam[19] as a localized heat source. In this type of patterning, the use of the liquid metal carboxylate precursors provides the advantage that thicker features may be grown because the precursor can flow into the area where deposition is occuring. Therefore, rastering the beam across the desired feature after a slight delay for the precursor to reflood that area will allow thicker films to be developed. The preparation of copper wires by laser pyrolysis of $Cu(MEEA)_2$ in this manner has already been achieved.[20]

The liquid metal carboxylates may also be used to synthesize ceramics by a modified powder process. One of the main advantages that chemical routes to ternary metal oxide ceramics have over the conventional method of preparation from the separate metal oxide powders is the ability to achieve a much more homogeneous mixture of the two metal ions. This results in a much smaller distance over which the metal ions must diffuse in order to form the desired phase and in turn leads to lower preparative temperatures and quicker reaction rates. A simple application of the liquid metal carboxylates to achieve more homogeneous ceramic precursor would be to use one liquid salt to coat another metal oxide powder with a second metal oxide film. This approach is shown schematically in Fig. 1 in comparison to conventional powder processing. For example, nickel ferrite was prepared by using $Ni(MEEA)_2 \cdot 0.5H_2O$ to coat Fe_2O_3 powders with a continuous film of NiO. Upon heating this material to 800°C, a remarkable solid-state reaction occurred to puff the precursor particles into broccoli flower-like collections of very small particles.[4]

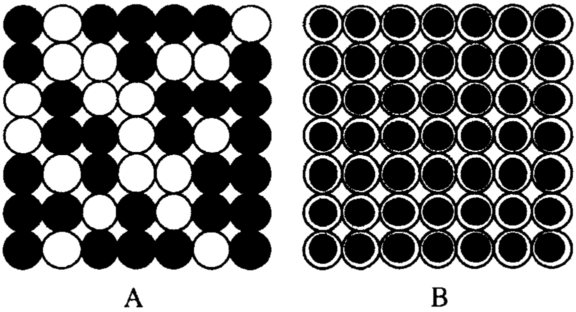

FIGURE 1 Metal oxide distribution in (A) conventional powder processing and (B) modified powder processing with liquid carboxylates

Since the liquid metal carboxylates have proven very useful for the preparation of inverse spinels such as $NiFe_2O_4$, it was very likely that they would also be useful for the synthesis of the parent spinel, $MgAl_2O_4$ and other aluminum-containing ceramics. The target ceramics have a wide range of applications in the areas of wear-resistant coatings, composites, structural materials, optics, and electronics. For example, $MgAl_2O_4$ is used extensively as a refractory material in the ceramic industry because of its low density and high stability in harsh environments.[21] Also, its good resistance to damage by radiation, such as swelling or degradation of strength, makes it useful as an insulating material for fusion reactor cores.[22] Spinel also shows promise for use in electronic applications[23,24] such as humidity sensors and as an optical material that is transparent in the visible and the 3–5 μm infrared regions.[25–27] Other aluminum spinels, MAl_2O_4 where M is a divalent transition metal, are important catalysts and absorbants.[28] Yttrium aluminum garnet (YAG), $Y_3Al_5O_{12}$ has been used widely as a laser host material[29] and is very useful in the form of coatings or bodies for high-temperature applications.[30] In structural ceramics, YAG may be used as either a monolithic body or as the matrix phase in composite materials.[30] Aluminosilicates such as mullite, $Al_6Si_2O_{13}$, are important refractory ceramics that are widely used as structural ceramics, electronic substrates, turbine engine components, protective coatings, and infrared transmitting windows.[31]

SYNTHESIS AND PROPERTIES OF MEEA SALTS

Typically, metal carboxylates are synthesized by reaction of the carboxylic acid with a metal carbonate or hydroxide or by a metathesis reaction between an ammonium or alkali metal salt of the carboxylate and a metal chloride or nitrate. The latter method is inappropriate for synthesis of MEEA salts because of the extreme difficulty of removing salts such as ammonium or sodium chloride or nitrate from the liquid metal carboxylate. Not only will the metal carboxylate dissolve these salts, but it will also solubilize them in non-aqueous solvents. Therefore, the synthesis of aluminum and magnesium MEEA salts was achieved by different means. $Mg(MEEA)_2 \cdot 2H_2O$ was readily prepared by reaction of magnesium hydroxide with two equivalents of MEEAH in water. The liquid dihydrate was obtained upon drying the product in vacuo over P_2O_5 at ambient temperature, while the anhydrous compound was obtained as a glassy, plastic solid by drying in vacuum at 100°C. $Y(MEEA)_3 \cdot 5.3H_2O$ was obtained as a pale yellow liquid from the reaction of yttrium carbonate with MEEAH in water followed by drying under vacuum at room temperature.[32] The reaction of $Al(OH)_3$ with MEEA was found to be unacceptably slow and, therefore, the synthesis of $Al(MEEA)_3$ was attempted using the reaction of aluminum isopropoxide with three equivalents of HMEEA in dry ethanol. This reaction was found to be accompanied by a side reaction that produces one equivalent of the ethyl ester of 2-[2-(2-methoxyethoxy)ethoxy] acetic acid and one equivalent of hydroxide per aluminum ion [Eq. (1)].[33] The latter reaction is not surprising since the interaction of metal alkoxides with carboxylic acids often results in such esterification reactions.[34,35]

$$Al(OEt)_3 + 3RCO_2H \longrightarrow (RCO_2)_2AlOH + RCO_2Et + 2\,EtOH \quad (1)$$

Thus, the product obtained, $Al(MEEA)_2OH{\cdot}H_2O$ has a formula similar to other well-known basic aluminum carboxylates such as $Al(O_2CH_3)_2OH{\cdot}xH_2O$. Fortunately, the generation of aluminum hydroxide linkages does not have a detrimental effect on the physical properties of the aluminum carboxylate which retains its liquid nature. Also, the similarity between the formulas of the acetate and MEEA salts suggested that the latter compound could be readily obtained from the former via a transacylation reaction in water that could be driven to completion by removal of the volatile acetic acid [Eq. (2)]. This reaction was found to be a rapid and extremely convenient and inexpensive method for the preparation of $Al(MEEA)_2OH{\cdot}H_2O$.

$$(CH_3CO_2)_2AlOH + 2\,HMEEA \rightarrow (MEEA)_2AlOH + 2\,CH_3CO_2H \qquad (2)$$

The infrared spectra of the yttrium, magnesium and aluminum salts of MEEA clearly indicate the presence of both monodentate and bridging carboxylates (Table I). The presence of monodentate carboxylates is unusual since most yttrium, magnesium and aluminum[36] carboxylate complexes have bridging, bidentate carboxylic acids. The observance of monodentate carboxylates is indicative of the strong chelation of the aluminum and magnesium ions by the ether oxygens of the MEEA ligand. These vibrational frequencies are also dependant on the degree of hydration. For example, anhydrous $Mg(MEEA)_2$ showed only a weak absorption for monodentate carboxylate, and the symmetrical stretch for the bridging carboxylate was significantly lower in frequency than that of the dihydrate (Table I). This result suggests that the water molecules of the dihydrate are bound to the magnesium ion in $Mg(MEEA)_2{\cdot}2H_2O$ and dehydration therefore leads to increased bridging and stronger bonding of the MEEA ligands to the metal ions.

^{13}C NMR spectroscopy (Table II) shows that there is only one type of MEEA ligand environment for $Y(MEEA)_3{\cdot}5.3H_2O$, $Al(MEEA)_2(OH){\cdot}H_2O$ or $Mg(MEEA)_2{\cdot}2H_2O$ when they are dissolved in chloroform, acetonitrile, or water. Therefore, it may be presumed that either exchange is rapid on the NMR timescale between both modes of carboxylate coordination or the structures of the metal complexes are changed in solution. The ^{13}C NMR spectrum of $Al(MEEA)_2(OH){\cdot}H_2O$ as a neat liquid actually does show two ligand environments (Table II). For example, the carboxylate carbons give rise to a major resonance at 177.8 ppm and a minor one at 172.5 ppm.

TABLE I Carboxylate stretching frequencies (cm^{-1})

Compound	ν *monodentate*	ν_{as} *bridging*	ν_s *bridging*
$Al(MEEA)_2OH{\cdot}H_2O$	1745 (s)	1628 (s)	1473 (s)
$Mg(MEEA)_2{\cdot}2H_2O$	1751 (m)	1612 (s)	1454 (s)
$Mg(MEEA)_2$	1725 (w)	1617(s)	1429 (s)
$MgAl_2(MEEA)_4(OH)_2(NO_3)_2$	1745 (w)	1628 (s)	1475 (m)
$Mg_2Al(MEEA)_2(OH)(NO_3)_4$	1763 (w)	1628 (m)	1475 (m)
$Y(MEEA)_3{\cdot}5.3H_2O$	1733 (w)	1615 (s)	1386 (s)
$Y_3Al_5(MEEA)_9(NO_3)_{15}{\cdot}49H_2O$	1761 (w)	1638 (m)	1380 (s)

TABLE II ^{13}C NMR chemical shifts (ppm) in $CDCl_3$

Compound	CO_2	OCH_2CO_2	CH_3O	OCH_2CH_2O
$Al(MEEA)_2OH{\cdot}H_2O$	177.3	71.6	58.5	70.0
$Mg(MEEA)_2{\cdot}2H_2O$	176.5	71.8	59.8	70.3
$Mg(MEEA)_2$	177.3	71.6	58.5	70.0
$Y(MEEA)_3{\cdot}5.3H_2O$	177.2	71.5	58.6	70.1
$Al(MEEA)_2OH{\cdot}H_2O$*	177.8, 172.5	71.9	58.4, 57.2	70.3
$MgAl_2(MEEA)_4(OH)_2(NO_3)_2$*	178.6, 174.9	71.2	58.2	69.6

* Neat liquids.

The ^{27}Al NMR spectrum of $Al(MEEA)_2(OH){\cdot}H_2O$ exhibits a relatively sharp peak with the highly unusual chemical shift of −59 ppm. Presumably, this resonance is due to six-coordinate aluminum, and the fact that it occurs out of the normal chemical shift range of six-coordinate aluminum (−20 to −45 ppm[37]) may be due to unusual shielding of the aluminum nuclei by the carboxylate moieties. Similar, unexplainably high-field chemical shifts are observed for aluminum organophosphates ($\delta = -20$ to -17 ppm) and AlI_4^- ($\delta = -27$ ppm).[37] An alternative explanation would be that the aluminum ion is seven- or eight-coordinate (since chemical shifts of aluminum progress towards higher field with increase in coordination number[37]), but, considering the extremely small size of aluminum, this is not very probable. Notably, when dissolved in $CDCl_3$, this complex shows a more "normal" chemical shift of 19 ppm.

The thermal decomposition of the MEEA salts occurs over the range of 170–400°C. For example, the thermal gravimetric analysis trace of $Al(MEEA)_2OH{\cdot}H_2O$ is shown in Fig. 2. The MEEA ligand does not pyrolyze cleanly, and the high temperature for complete organic burnout is due to the intermediate formation of pyrolytic carbon. For some metals (e.g., Ni, Al, and Cr) the decomposition is also accompanied by volatilization of some metal complex (possibly the MEEA salt itself). Unfortunately, appreciable volatility is only realized at the decomposition temperature so that the application of these compounds in chemical vapor deposition is unlikely. Nevertheless, allowance must be made for the loss of some metal when preparing multimetallic ceramics. This is readily achieved by determining the ceramic yield from the MEEA precursor under the same conditions (e.g., ramp rate and pyrolysis temperature) as those used for the ceramic synthesis, and then using these numbers to calculate the stoichiometry of the reactants. The ceramic products obtained at 500°C from $Mg(MEEA)_2{\cdot}2H_2O$ and $Y(MEEA)_3{\cdot}5.3H_2O$ are MgO and $Y_2O_2CO_3$, respectively. The formation of the latter phase indicates that the application of these metal carboxylates for the preparation of metals oxides in which the metal forms a refractory carbonate will be complicated by the formation of intermediate carbonate phases. The thermal decomposition of $Al(MEEA)_2(OH){\cdot}H_2O$ in air at 500°C produces an amorphous material that converts to γ-alumina upon heating to 700°C.

SYNTHESIS OF ALUMINUM SPINELS USING MEEA SALTS

The synthesis of the parent spinel, $MgAl_2O_4$, using liquid metal carboxylates could potentially be realized by the "solution" route using either a mixture of magnesium nitrate in an aluminum MEEA salt or a solution of aluminum nitrate in $Mg(MEEA)_2$ or by the modified powder process using appropriate mixtures of either aluminum or magnesium carboxylates with magnesium oxide or aluminum oxide, respectively.

A mixture of the magnesium and aluminum liquid metal carboxylates can serve as a good precursor for spinel, but a more economical precur-

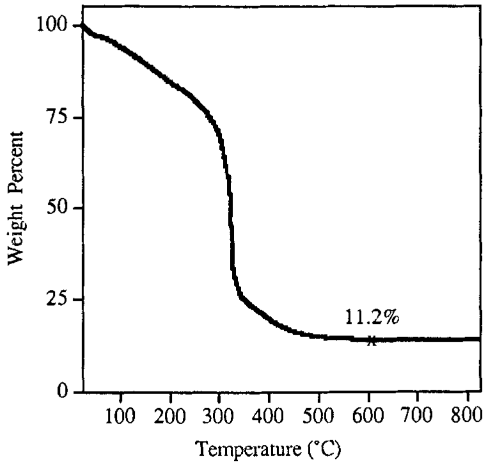

FIGURE 2 TGA trace for $Al(MEEA)_2(OH){\cdot}H_2O$ in air (5°C/min)

sor was prepared by dissolving a half-molar equivalent of magnesium nitrate in $Al(MEEA)_2(OH){\cdot}H_2O$. The magnesium salt was found to dissolve readily with gentle heating to afford a colorless liquid. Drying in vacuo at room temperature to remove the water introduced as the magnesium's waters of hydration yielded a white, amorphous solid with the formula $MgAl_2MEEA)_4(OH)_2(NO_3)_2{\cdot}2H_2O$. Apparently, the coordination of the magnesium ions by the MEEA ligands (through chelation by the ether oxygen atoms) is strong enough that most of the waters of hydration are readily displaced. Infrared spectroscopy demonstrates a marked diminishment in the proportion of the MEEA ligand that is unidentate as compared to that observed for $Al(MEEA)_2(OH){\cdot}H_2O$ (Table I). This likely results from the increased demands on the ligand to coordinatively saturate both the magnesium and aluminum ions. The infrared absorptions of the nitrate ions (observed at $v_1 = 1248$ cm^{-1} and $v_2 = 1979$ cm^{-1}) are indicative of a chelating bidentate mode of coordination.[38] The ^{13}C NMR of the neat spinel precursor also shows marked changes from that of $Al(MEEA)_2(OH){\cdot}H_2O$ (Table II). In particular, there is a marked increase in the intensity of the higher field carboxylate resonance. In keeping with the observed changes in the infrared spectra, the latter resonance may therefore be attributed to bidentate, bridging carboxylates. By default, the downfield peak may therefore be assigned to a unidenate carboxylate environment. The dissolution of magnesium nitrate in $Al(MEEA)_2(OH){\cdot}H_2O$ also caused profound changes in the ^{27}Al NMR spectra of the neat liquids. The resonance at –59 ppm became very diminished in intensity and shifted slightly downfield to –51 ppm. At the same time, a new intense peak attributable to six-coordinate aluminum was observed at –0.4 ppm.

Thermal gravimetric analysis of this liquid spinel precursor indicated that the material dehydrated at 140°C, and it was found that the material liquified at this point. Furthermore, the material remained liquid upon cooling to room temperature. It is highly unusual that an anhydrous compound be a liquid while the corresponding hydrate is a solid, and this atypical behavior must be due to strong hydrogen bonding when the water is present. When the hydrated compound was further heated in the TGA experiments, it was found that the organic and nitrate ions burned out over the range of 175 to 600°C (Fig. 3). The mass at 600°C corresponds to the expected ceramic yield of $MgAl_2O_4$. However, the XRD pattern of the material from bulk pyrolysis of the precursor at this temperature shows that it is fairly amorphous, exhibiting only an extremely broad reflection centered at $2\theta = 32°$ (Fig. 4). Further heating resulted in the gradual crystallization of spinel. The presence of crystalline spinel is evident at 700°C, but grain growth is very sluggish so that sharp reflections are only observed in samples heated above 900°C. There was no evidence for the presence of any other magnesium or aluminum-containing phases. Therefore, this liquid precursor is unusual in the fact that it may be used to generate an amorphous solid solution of magnesium and aluminum oxide which may subsequently be converted to a spinel of varying crystallinity depending on sintering temperature. Therefore, it will likely be possible to generate oxide films with adjustable physical properties by spin-coating this precursor on substrates and sintering at varying temperatures. Also, it is very probable that the amorphous to crystalline phase change will be very susceptible to epitaxy so that epitaxial $MgAl_2O_4$ films may be preparable.

Similar results were obtained for the synthesis of $NiAl_2O_4$ and $CuAl_2O_4$ from precursors prepared by dissolution of either nickel or copper nitrate in the liquid aluminum precursor. However, these materials were significantly more crystalline at lower temperatures, a reflection of the greater mobility of the Ni^{2+} and Cu^{2+} ions as compared to Mg^{2+}.

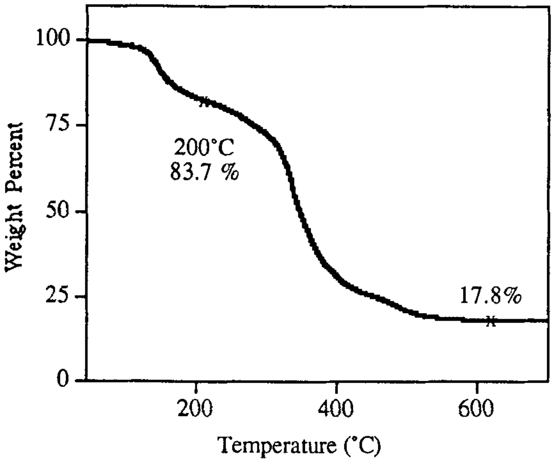

FIGURE 3 TGA trace for $MgAl_2(MEEA)_4(OH)_2(NO_3)_2 \cdot 2H_2O$ in air (5°C/min)

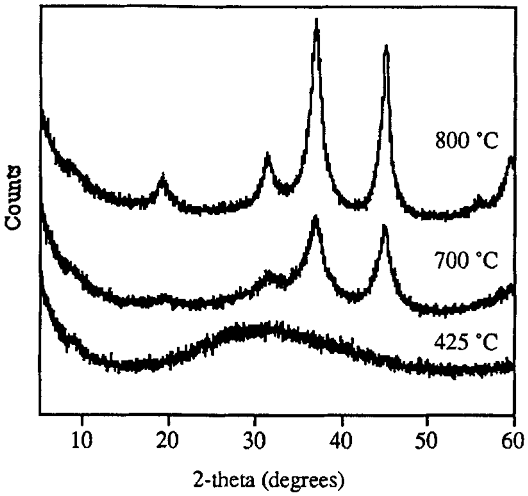

FIGURE 4 XRD Patterns of $MgAl_2(MEEA)_4(OH)_2(NO_3)_2 \cdot 2H_2O$ fired at various temperatures

A precursor for $MgAl_2O_4$ could also potentially be prepared by dissolving two equivalents of aluminum nitrate hexahydrate in $Mg(MEEA)_2 \cdot 2H_2O$. It was found that this was most easily done by dissolving the aluminum nitrate in a sufficient amount of water to allow deliquescence and mixing the resulting liquid with $Mg(MEEA)_2 \cdot 2H_2O$. This yielded a viscous liquid which, upon attempted drying, evolved nitrous oxide from decomposition of the nitrate ion. This may have resulted from oxidation of the MEEA ligand, but more likely occurred as a consequence of the known decomposition of hydrated aluminum salts upon dehydration.[28] Whatever the cause, drying at 100°C yielded a glassy, foamed solid that had a much reduced nitrogen content but still retained MEEA ligands. $MgAl_2O_4$ powders could be prepared from this solid, but this precursor was not processible into films or fibers. The difference between the two solution-type precursors for $MgAl_2O_4$ suggests that, in the case of magnesium and aluminum, ligand transfer reactions between the two metals does not occur. This was borne out by the infrared spectrum of $MgAl_2MEEA)_4(OH)_2(NO_3)_2 \cdot 2H_2O$ which has carboxylate stretches that are very similar to the $Al(MEEA)_2(OH) \cdot H_2O$ starting material and different from those of $Mg(MEEA)_2 \cdot 2H_2O$.

The preparation of $MgAl_2O_4$ by a modified powder process was found to also occur quite readily and yielded crystalline spinel at comparable temperatures to the nitrate solution routes. Chromatographic γ-alumina was mixed well with $Mg(MEEA)_2 \cdot 2H_2O$ by stirring the reactants together in an alumina crucible. The XRD pattern of this mixture after firing at 700°C demonstrated the presence of spinel along with a small amount of magnesium oxide. The formation of the latter phase is likely due to deposited MgO that did not coat onto the alumina phase. This result is in sharp contrast to the preparation of $NiFe_2O_4$ from $Ni(MEEA)_2 \cdot 0.5H_2O$ and Fe_2O_3 where the ferrite was obtained cleanly.[4] A likely cause for this difference is the fact that $Ni(MEEA)_2 \cdot 0.5H_2O$ is slightly volatilized upon pyrolysis while the magnesium salt is non-volatile. Thus, an in situ CVD reaction could lead to better coating of nickel oxide on the iron oxide substrate than that which occurs for the spinel precursor. Nevertheless, the modified powder process does produce spinel at remarkably lower temperatures than traditional powder processing which requires temperatures in excess of 1200°C.

SYNTHESIS OF OTHER ALUMINUM CERAMICS USING MEEA SALTS

A precursor for yttrium aluminum garnet was previously prepared by dissolving an appropriate quantity of hydrated aluminum nitrate in $Y(MEEA)_3 \cdot 5.3H_2O$.[32] Due to the high viscosity of the latter material, the mixing of these salts was more readily achieved by employing a small amount of water to disperse the reagents. Drying the resulting solution in vacuo at 60°C yielded a colorless liquid with the formula $Y_3Al_5(MEEA)_9(NO_3)_{15} \cdot 49H_2O$. Infrared spectroscopy demonstrated only a small change in the infrared spectrum of $Y(MEEA)_3 \cdot 5.3H_2O$ when $Al(NO_3)_3 \cdot 9H_2O$ is dissolved in it (Table I), suggesting that the MEEA ligands remain coordinated to yttrium.

Thermal gravimetric analysis of the liquid YAG precursor (Fig. 5) indicated a fairly complicated decomposition pattern that culminated in the formation of a white solid with a mass that corresponded to $Y_3Al_5O_{12}$ at 425°C. The material from bulk pyrolysis of the precursor at 500°C shows that it is fairly amorphous, exhibiting only an extremely broad reflection centered at $2\theta = 31°$ (Fig. 5). Further heating to 600°C results in the crystallization of YAG, a process which is complete at 800°C (Fig. 6). Thus, this precursor yields yttrium aluminum garnet at a temperature 100°C lower than that previously achieved by sol-gel.[30]

In order to determine the extent to which magnesium nitrate can be dissolved in $Al(MEEA)_2(OH) \cdot H_2O$, a potential precursor for the layered double hydroxide, $Mg_4Al_2(OH)_{14}$, was prepared by dissolving two molar equivalents of magnesium nitrate in the liquid aluminum carboxylate. The resulting product was a viscous liquid that had an infrared spectrum very similar to that of the spinel precursor, $MgAl_2MEEA)_4(OH)_2(NO_3)_2 \cdot 2H_2O$ (Table I). Like the latter precursor, an amorphous oxide phase was obtained upon pyrolysis of $Mg_2Al(MEEA)_2(OH)(NO_3)_4 \cdot xH_2O$ at 500°C. The composition of this solid corresponded to $Mg_4Al_2O_7$, and upon further heating, spinel starts to crystallize at 600°C. By 700°C, the solid separates into both a spinel phase and periclase (MgO). While the precursor does not yield the double hydroxide directly, it is possible that the amorphous phase could be converted to the desired product by hydrothermal treatment. Nevertheless, the ability to prepare amorphous or metastable phases using the MEEA salts is well demonstrated by this precursor.

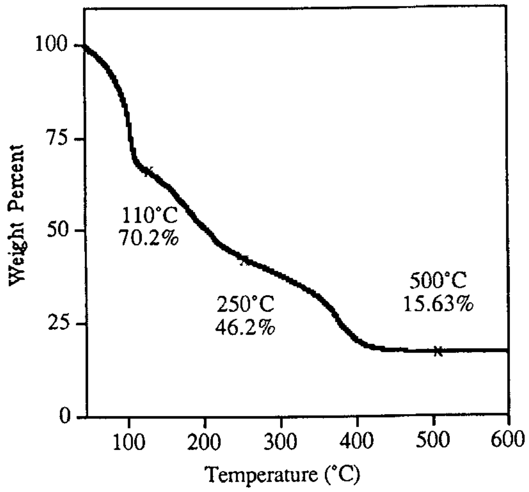

FIGURE 5 TGA Trace for $Y_3Al_5(MEEA)_9(NO_3)_{15}\cdot 49H_2O$ in air (5°C/min)

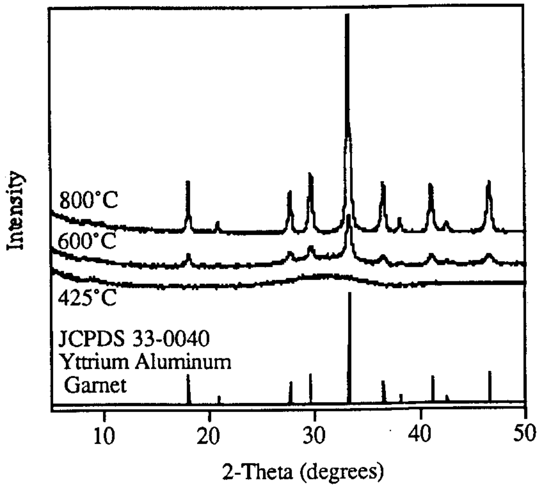

FIGURE 6 XRD patterns of $Y_3Al_5(MEEA)_9(NO_3)_{15}\cdot 49H_2O$ fired at various temperatures compared to JCPDS pattern for YAG

The success of the $Mg(MEEA)_2/Al_2O_3$ precursor for synthesis of spinel suggests that even more remarkable results could be realized by use of a colloidal or nano-sized oxide phase rather than larger particles. Therefore, an aluminosilicate precursor for $Al_6Si_5O_{19}$ was prepared by dissolving $Al(MEEA)_2OH$ in a 30 weight percent aqueous solution of a colloidal silica (LUDOX® AM-30). After removal of water in vacuum at room temperature, a perfectly clear liquid was obtained that showed no tendency to precipitate the silica phase. The liquid could be converted to a slightly sticky, moldable solid by pyrolysis in air at 150°C. A transparent, glassy, amorphous oxide phase resulted from heating the precursor to 500°C. This glass remained a non-crystalline aluminosilicate upon heating as high as 1100°C. The extent to which a liquid precursor could be prepared was probed by preparing a precursor with the ratio of six molar equivalents of SiO_2 per mole of $Al(MEEA)_2OH$. Removal of water from this mixture yielded a perfectly clear semi-fluid gel. Unlike the higher aluminum-to-silicon ratio precursor, this compound yields an opaque amorphous solid after burn out of the organics and then forms weakly crystalline mullite ($Al_6Si_2O_{13}$) and tridymite (SiO_2) after heating to 1100°C. On the other hand, a liquid precursor prepared with the mullite stoichiometry yields a significantly more crystalline material at 1100°C, but it contains a complex mixture of aluminosilicates none of which is mullite. Therefore, while liquid precursors for aluminosilcates are readily prepared, the solid state chemistry of the resulting oxides is extremely complicated. Nevertheless, at reasonably low temperature, nano-composite alumina/silica ceramics and coatings may be readily prepared.

CONCLUSIONS

The metal salts of 2-[2-(2-methoxy)ethoxy]ethoxyacetate, because, of their liquid nature and good solvent properties, have significant applications in the preparation of oxide materials. There is considerable flexibility in the preparation of precursors for multimetallic oxides since the liquid metal carboxylates may be mixed in any ratio or one or more metals can be supplied as a nitrate or acetate salts or as nano-particulate oxides without losing the fluidity of the precursor. The precursors may be converted to ceramic films by painting or dip- or spin-coating the neat precursors or on appropriate substrates and followed by firing at temperatures ranging from 500°C to 1100°C depending on the target ceramic and the desired crystallinity. The liquid metal carboxylates have also been demonstrated to be quite useful for the preparation of bimetallic ceramics via a modified powder process. Aside from the synthetic potential of such reactions, they may also be applicable to mechanistic investigations of solid state metal oxide reactions and the preparation of supported catalysts. Finally, the melding of nano-technology with metallo-organic deposition has opened up numerous exciting possibilities for the preparation of metal oxides with a high ceramic yield and nano-composite materials.

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