

# Preparation of Nickel Ferrite Using Liquid Metal Carboxylates

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Unusual metal carboxylates that are liquids at room temperature have been synthesized and applied to the preparation of nickel ferrite. These salts  $\text{Ni}(\text{MEEA})_2 \cdot 0.5\text{H}_2\text{O}$  and  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot 5.5(\text{H}_2\text{O})$  bear the polyether carboxylate anion 2-[2-(2-methoxyethoxy)ethoxy]acetate ( $\text{MEEA} = \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CO}_2^-$ ). They may be utilized for the low-temperature preparation of nickel ferrite by using  $\text{Ni}(\text{MEEA})_2 \cdot 0.5\text{H}_2\text{O}$  to coat  $\text{Fe}_2\text{O}_3$  powders with a continuous film of NiO. Upon heating this material to 800 °C, a remarkable solid-state reaction occurs to puff the precursor particles into broccoli floret-like collections of very small particles. A homogeneous precursor solution for nickel ferrite may be prepared via dissolution of  $\text{Ni}(\text{NO}_3)_2$  in  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot 5.5(\text{H}_2\text{O})$ . This precursor solution yields a metastable amorphous  $\text{NiFe}_2\text{O}_4$  phase at 300 °C which undergoes an exothermic crystallization at 374 °C with an energy change of  $-126.1$  kJ/mol.

## Introduction

Spinel ferrites,  $\text{MFe}_2\text{O}_4$  (M = Mg, Mn, Fe, Co, Ni, Zn, Cu, Cd, etc.), combine a wide range of useful magnetic properties with relatively low electrical conductivity. Thus, unlike magnetic metals and alloys, they display low eddy current loss in alternating current applications and they are particularly useful in the radio frequency range. Therefore, the spinel ferrites have numerous applications in recording heads, core materials for various transformers, inductors, and TV deflection units, and in recording tape.<sup>1</sup> Typically, ferrites are prepared by reacting intimate mixtures of the constituent metal oxides or carbonates. The shortcomings of such an approach include the formation of relatively coarse particles leading to large and inhomogeneous porosity in sintered bodies, incomplete reaction of the oxide powders, and limitations on the ability to control composition.<sup>2</sup>

Metal carboxylates have been used in a variety of improved synthetic routes to ferrites. For example, solid solutions of  $\text{Fe}^{2+}$  and  $\text{M}^{2+}$  may be coprecipitated from solution by treatment with oxalic acid.<sup>3</sup> These precipitates may then be converted to ferrites by heating to temperatures between 800 and 1000 °C. Another example of metal carboxylate precursors for stoichiometric ferrites are the mixed acetates,  $\text{M}_3\text{Fe}_6(\text{CO}_2\text{CH}_3)_{17}\text{O}_3(\text{OH}) \cdot 12\text{pyridine}$  (M = Ni, Co, Mn), reported by Wickham et al.<sup>4</sup> More recently,  $[\text{Ni}(\text{H}_2\text{O})_6][\text{FeCl}(\text{EDTA})\text{H}]_2 \cdot 4\text{H}_2\text{O}$  was described as a preceramic com-

pound which yields highly stoichiometric nickel ferrite at 900 °C.<sup>5</sup>

Recently, we<sup>6</sup> have discovered an intriguing class of metal carboxylates that have the highly unusual property of being liquids at room temperature. These carboxylates have polyether linkages {e.g. 2-[2-(2-methoxy)ethoxy]ethoxyacetate ( $\text{MeOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CO}_2^-$ , MEEA)} which undoubtedly contribute to the unusual characteristics of the metal salts by chelating and “solvating” the metal ions. In this investigation, the MEEA salts of nickel and iron have been found to be room-temperature liquids and their application to the synthesis of nickel ferrite is reported herein.

## Experimental Section

Nickel hydroxide (MCB), nickel nitrate hexahydrate (Mallinckrodt), deuterium oxide (Aldrich), and ferric chloride hexahydrate (Strem) were commercial reagents and were used without further purification. The  $\text{Fe}_2\text{O}_3$  (hematite) used was a very fine powder (Densfil) and was obtained as a gift from Densimix, Inc. Amberlite IRA-440C (Sigma) ion-exchange resin was washed copiously with water before use. Infrared spectra were obtained as KBr pellets on a Mattson Cygnus 100 FT-IR spectrometer. UV-visible spectra were obtained using aqueous solutions and a Hewlett-Packard 8451A diode array spectrometer. Thermogravimetric studies were performed using 20–30 mg samples in a Seiko TG/DTA 220 instrument under a 100 mL/min flow of dry air. The temperature was ramped from 25 to 625 °C at a rate of 2 °C/min while the off-gases were analyzed on a Fisons Thermolab mass spectrometer. Bulk pyrolyses at various temperatures were performed in ambient air in a temperature-programmable muffle furnace using ca. 2 g samples, a temperature ramp of 5 °C/min, and a hold time of 12 h. X-ray powder diffraction patterns were obtained on a Scintag XDS 2000 diffractometer

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using copper K $\alpha$  radiation. Microanalysis for carbon and hydrogen content was performed by Tulane's Coordinated Instrument Facility. Chloride concentrations were determined using a chloride ion selective electrode that had been calibrated using NIST-traceable standards.

**Preparation of Ni(MEEA) $_2$ ·0.5H $_2$ O.** A mixture of Ni(OH) $_2$  (4.737 g, 51.09 mmol) and 2-[2-(2-methoxyethoxy)ethoxy]acetate (HMEEA) (18.19 g, 102.1 mmol) in 25 mL of water was heated at reflux until the Ni(OH) $_2$  completely dissolved (ca. 2 h). The resulting pale green solution was concentrated on a rotary evaporator and was then finally dried at 100 °C under oil pump vacuum. The yield of Ni(MEEA) $_2$ ·0.5H $_2$ O as a somewhat viscous green liquid was 21.22 g (98.5%). CH analysis calculated for C $_{28}$ H $_{54}$ O $_{21}$ Ni $_2$ (%): C 39.84; H 6.45. Found: C 39.99, H 6.68. IR (cm $^{-1}$ ) (neat film on KBr plates): 3394 (br, s), 2889 (s), 2598 (sh), 2528 (m), 1736 (s), 1653 (s), 1593 (sh), 1508 (w), 1456 (sh), 1419 (s), 1354 (sh), 1332 (m), 1294 (w), 1248 (m), 1199 (m), 1107 (s), 1028 (sh), 949 (m), 887 (sh), 848 (m), 775 (m), 727 (m), 669 (m), 603 (m), 551 (sh), 464 (m).

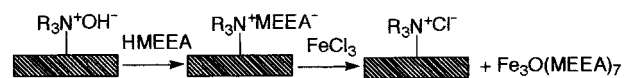
**Preparation of Fe $_3$ O(MEEA) $_7$ ·5.5H $_2$ O.** The hydroxide form of IRA-440C anionic ion-exchange resin (87.49 g, 385.0 mequiv OH $^{-}$ ) was reacted with a 20% excess of HMEEA in 100 mL of water. The resin was isolated by filtration and washed copiously with water (3  $\times$  100 mL). It was then added to a solution of FeCl $_3$ ·6H $_2$ O (9.214 g, 34.09 mmol) so that there was a 10% molar excess of MEEA anions to iron. After stirring for 1 h, the deep red solution was filtered and concentrated by rotary evaporator. Final drying of the product was performed under oil pump vacuum in a vacuum desiccator over phosphorus pentoxide. The final yield was 9.45 g (54.9%) of Fe $_3$ O(MEEA) $_7$ ·5.5H $_2$ O as a dark-red viscous liquid. Analysis calculated for C $_{98}$ H $_{204}$ O $_{93}$ Fe $_6$  (%): C 38.65; H 6.75; Fe 11.00. Found: C 38.88; H 6.82; Fe, 10.99. IR (cm $^{-1}$ ) (neat film between KBr plates): 3447. (br, s), 2899 (s), 2631 (sh), 1741 (s), 1618 (s), 1456 (s), 1419 (sh), 1356 (sh), 1332 (s), 1290 (sh), 1246 (m), 1201 (m), 1105 (s), 1026 (m), 935 (m), 850 (m), 709 (m), 667 (m), 588 (m).

**Preparation of Fe $_3$ O(MEEA) $_7$ ·5.5D $_2$ O.** Fe $_3$ O(MEEA) $_7$ ·5.5H $_2$ O (0.10 g) was dissolved in 2 mL of deuterium oxide (99.9 atom % D). After 2 h the solvent was removed completely in vacuo. This was repeated two more times. IR (cm $^{-1}$ ) (neat film between KBr plates): 2902 (s), 2507 (br), 2057 (w), 1738 (s), 1620 (s), 1454 (s), 1419 (sh), 1354 (sh), 1329 (w), 1257 (m), 1199 (w), 1157 (sh), 1094 (br), 1020 (sh), 961 (w), 934 (m), 858 (s), 709 (m), 659 (w), 600 (w), 555 (w), 508 (w), 473 (w).

**Preparation of NiFe $_2$ O $_4$  from Ni(MEEA) $_2$ ·0.5H $_2$ O and Fe $_2$ O $_3$ .** Ni(MEEA) $_2$ ·0.5H $_2$ O (2.580 g, 39.0 mmol) and Fe $_2$ O $_3$  were well-mixed in an alumina crucible using a glass rod. The material thus obtained was heated in a muffle furnace in ambient air to 500 °C. At this point a black solid (0.902 g, 28.3%) was isolated and characterized by SEM and XRD. A portion of it (0.500 g) was replaced in the muffle furnace and heated to 800 °C. No weight-loss was observed and this sample was also characterized by SEM and XRD.

**Preparation of NiFe $_2$ O $_4$  from Fe $_3$ O(MEEA) $_7$ ·5.5H $_2$ O and Ni(NO $_3$ ) $_2$ ·6H $_2$ O.** Ni(NO $_3$ ) $_2$ ·6(H $_2$ O) (0.48 g, 1.65 mmol) was added to Fe $_3$ O(MEEA) $_7$ ·5.5H $_2$ O (1.657 g, 1.093 mmol) and the mixture was stirred until the nickel nitrate had dissolved. The mixture was dried in a vacuum (10 $^{-3}$  Torr) at room temperature to yield 1.85 g (98.6%) of [Fe $_3$ O(MEEA) $_7$ ] $_2$ [Ni(NO $_3$ ) $_2$ ] $_3$ ·2H $_2$ O as a reddish brown liquid. Elemental analysis calculated for C $_{98}$ H $_{186}$ N $_6$ O $_{92}$ Fe $_6$ Ni $_3$  (%): C 34.30; H 5.46; N 2.45. Found: C 34.42; H 5.54; N 2.53. IR (cm $^{-1}$ ) (neat film between KBr plates): 3431 (br), 2920 (s), 1645 (sh), 1624 (s), 1456 (s), 1429 (s), 1427 (sh), 1390 (m), 1370 (sh), 1330 (s), 1249 (m), 1201 (m), 1116 (s), 1114 (sh), 1026 (m), 931 (w), 912 (w), 846 (w), 787 (w), 713 (w), 617 (w), 493 (w).

This ferrite precursor (1.024 g) was heated in an alumina crucible muffle furnace in ambient air to 300 °C. At this point a black solid (1.85 g, 100% of the expected yield of NiFe $_2$ O $_4$ ) was isolated and characterized by XRD. Further heating to 400 °C resulted in no additional weight-loss and this sample was also characterized by XRD.



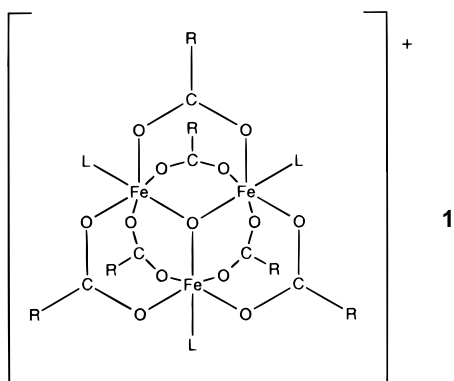
**Figure 1.** Preparation of FeO(MEEA) $_7$ ·5.5(H $_2$ O) via ion exchange.

## Results and Discussion

**Synthesis and Characterization of Liquid Metal Carboxylates.** The liquid metal carboxylates Ni(MEEA) $_2$ ·0.5H $_2$ O and Fe $_3$ O(MEEA) $_7$ ·5.5H $_2$ O were prepared by two different routes. The nickel salt could readily be obtained by reaction of nickel hydroxide and 2 equiv of 2-[2-(2-methoxyethoxy)ethoxy] acetic acid (HMEEA) in refluxing water. Removal of water by rotary evaporation at 1.9 Torr and 90 °C yielded a dark green liquid that contained half a water molecule per nickel atom. Thermal gravimetric analysis of this compound in air indicated that it decomposes in two steps which occur over the ranges 150–255 and 287–300 °C. The first step is thermoneutral and appears to be attributable to loss of water and a decomposition reaction of the ligand. The second weight loss is strongly exothermic and corresponds to oxidation of the remaining organics. The final ceramic yield after this step is 11.0%, and XRD analysis of a bulk sample of Ni(MEEA) $_2$ ·0.5H $_2$ O pyrolyzed at this temperature identified the final ceramic to be nickel oxide (JCPDS diffraction file 22-1189). On the basis of the formula of the nickel salt, the ceramic yield is lower than the expected one of 17.7%, and the pyrolysis of a bulk sample of the liquid nickel carboxylate also gave the same result. This fact may be attributed to volatilization of a small portion of the Ni(MEEA) $_2$  salt during the pyrolysis. We have previously observed volatilization of Cr(MEEA) $_3$  when HMEEA was prepared by oxidation of tris(ethylene glycol) methyl ether with chromic acid: even after distillation, the HMEEA contained traces of chromium. Similarly, when Ni(MEEA) $_2$ ·0.5H $_2$ O is heated in vacuo at 200 °C, a clear liquid distills which is green due to the presence of nickel. For the purposes of this investigation, an excess of the Ni(MEEA) $_2$  salt was used for the ferrite synthesis so that the observed ceramic yield corresponded to the required amount of nickel oxide for formation of NiFe $_2$ O $_4$  (see below). To ensure the volatilization of Ni(MEEA) $_2$  in the ferrite synthesis was commensurate with that in the pyrolysis of the pure nickel salt, identical heating programs were used for both pyrolyses.

An attempt was made to prepare Fe(MEEA) $_3$  from the reaction of FeCl $_3$ ·6H $_2$ O with 3 molar equiv of NaMEEA in water. However, it was discovered that the sodium chloride produced in the reaction was highly soluble in the desired iron MEEA salt. As a consequence, the isolated metal salt is highly contaminated with sodium chloride. Furthermore, the NaCl was solubilized in organic solvents by Fe(MEEA) $_3$  so that separation of the two materials proved very difficult. This complication was circumvented by using an anionic ion exchanger to prepare the iron salt (Figure 1). First, the hydroxide form of Amberlite IRA-440C ion-exchanger was reacted with HMEEA and then an excess of the resulting material was used to treat an aqueous solution of ferric chloride. This reduces the chloride concentration to 50.8 ppm. Removal of the water from this solution yielded a deep red liquid. After drying in vacuo over P $_2$ O $_5$  this

compound was found to be a basic carboxylate with the formula  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot 5.5\text{H}_2\text{O}$ . This composition, calculated from elemental analysis and dehydration experiments, is confirmed by the ceramic yield of  $\text{Fe}_2\text{O}_3$  in bulk pyrolysis experiments at 600 °C. This compound therefore appears to be similar to other basic carboxylates of iron<sup>7–10</sup> that have been previously reported such as  $[\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_6][\text{O}_2\text{CMe}] \cdot \text{H}_2\text{O}$ ,<sup>11</sup>  $[\text{Fe}_3\text{O}(\text{MeOH})_3(\text{O}_2\text{C}^t\text{Bu})_6][\text{O}_2\text{C}^t\text{Bu}]$ ,<sup>12</sup>  $[\text{Fe}_3\text{O}(\text{DMF})_3(\text{O}_2\text{CPh})_6][\text{O}_2\text{CPh}] \cdot \text{DMF}$ ,<sup>13</sup>  $[\text{Fe}_3\text{O}(\text{amino acid})_6(\text{H}_2\text{O})_3](\text{ClO}_4)_7$ ,<sup>14,15</sup>  $\text{Fe}_3\text{O}(\text{dicarboxylate})_3$  polymers,<sup>16</sup> and  $[\text{Fe}_3\text{O}(\text{TIEO})_2(\text{O}_2\text{CPh})_2\text{Cl}_3] \cdot 2\text{C}_6\text{H}_6$  (TIEOH = 1,1,2-tris(*N*-methylimidazol-2-yl)-1-hydroxyethane).<sup>17,18</sup> X-ray diffraction analysis of these compounds has revealed that the symmetric  $[\text{Fe}_3\text{O}(\text{L}_3(\text{O}_2\text{-CR})_6)]^+$  clusters have a common structural motif, **1**,



consisting of three iron atoms that lie at the apexes of an equilateral triangle with an oxygen atom in the middle. The carboxylate ions bridge the iron atoms so that each pair of iron atoms are connected by two bridges.

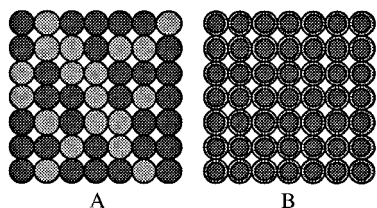
The similar composition of the iron MEEA salt to these basic carboxylates suggests that it may also have a similar trinuclear cluster. Matrix-assisted laser desorption (MALD) mass spectroscopy of  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot 5.5\text{H}_2\text{O}$  supports this contention since the largest observed fragment corresponds to  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot \text{H}_2\text{O}$  (*m/e* = 1441.3). The infrared spectra of  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot 5.5\text{H}_2\text{O}$  and  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot 5.5\text{D}_2\text{O}$ , however, indicates that the bonding in this cluster is different from that of the acetate. The deuterium oxide analogue was prepared so that the overlapping H–O–H bend of water would not interfere with interpretation of the carboxylate C–O stretch absorptions. The spec-

tra of these complexes as neat liquids clearly indicate the presence of both monodentate ( $\nu_{\text{as}} = 1741 \text{ cm}^{-1}$ ) and bridging ( $\nu_{\text{as}} = 1617 \text{ cm}^{-1}$  and  $\nu_{\text{s}} = 1456 \text{ cm}^{-1}$ ) carboxylates. The latter vibrational frequencies compare favorably to those of  $[\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_6]\text{Cl} \cdot 3\text{H}_2\text{O}$ <sup>19</sup> ( $\nu_{\text{as}} = 1595 \text{ cm}^{-1}$  and  $\nu_{\text{s}} = 1450 \text{ cm}^{-1}$ ) and may therefore be attributed to bridging carboxylates. However, the presence of monodentate carboxylates suggests a different structural motif for  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot 5.5\text{H}_2\text{O}$  than is observed for  $\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_7 \cdot \text{H}_2\text{O}$ . This is particularly true since the absorption of the monodentate carboxylates is much more intense than those of the bridging carboxylates. It is not surprising that the two clusters would be structurally different since the MEEA compound has numerous ether oxygens and a higher degree of hydration, all of which may contribute to the coordinative saturation of the iron atoms and prevention of formation of carboxylate bridges. By comparison, the less hydrated  $\text{Ni}(\text{MEEA})_2$  shows only IR absorptions for bidentate carboxylates ( $\nu_{\text{as}} = 1624 \text{ cm}^{-1}$  and  $\nu_{\text{s}} = 1456 \text{ cm}^{-1}$ ). Long et al. attributed a weak band at  $520 \text{ cm}^{-1}$  in  $[\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_6]\text{Cl} \cdot 3\text{H}_2\text{O}$  to the asymmetric stretch of the  $\text{Fe}_3\text{O}$  moiety,<sup>20</sup> and this band was also observed in the perchlorate derivative.<sup>16</sup> The infrared spectrum of the MEEA salt does not contain an absorption in this region, again suggesting a different structural motif. The stability toward hydrolysis of  $\text{Fe}_3\text{O}(\text{MEEA})_7 \cdot 5.5\text{H}_2\text{O}$  is another factor that differentiates it from other “ $\text{Fe}_3\text{O}$ ” basic carboxylates. The latter compounds tend to hydrolyze to give dimers such as  $\text{Fe}_6\text{O}_2(\text{OH})_2(\text{O}_2\text{-CR})_{12}$ <sup>21,22</sup> or larger clusters such as  $\text{Fe}_{11}\text{O}_6(\text{OH})_6(\text{O}_2\text{-CR})_{15}$ <sup>23,24</sup> while the MEEA compound may be dissolved in water without a change in its composition or molecular weight.

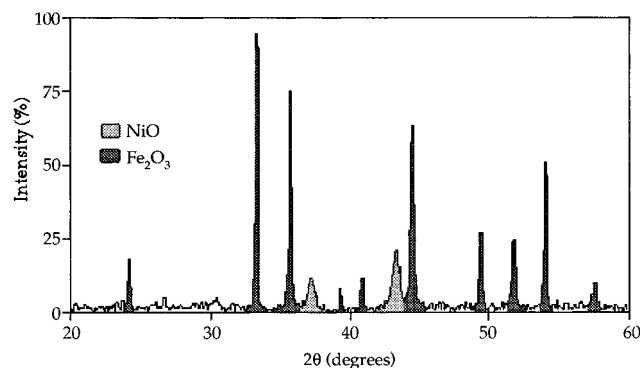
**Synthesis of Ferrites Using Liquid Metal Carboxylates.** One of the main advantages that chemical routes to ternary metal oxide ceramics have over the conventional method of preparation from the separate metal oxide powders is the ability to achieve a much more homogeneous mixture of the two metal 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 a more homogeneous ferrite precursor would be to use the liquid nickel salt to coat iron oxide powders with nickel oxide. This approach, shown schematically in Figure 2, is similar to a process developed by Rees and Carris for the thermally efficient preparation of barium titanate in which a monodispersed  $\text{TiO}_2$  powder was treated with an ammoniacal solution of elemental barium.<sup>25</sup> This gave a uniformly coated precursor powder that yielded crystalline  $\text{BaTiO}_3$  upon heating to 900 °C.

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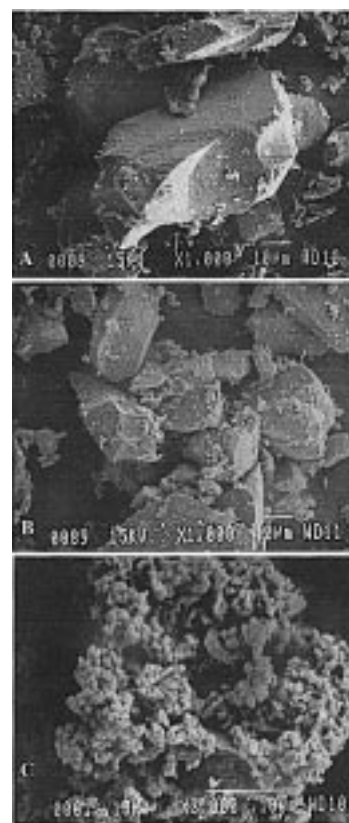
**Figure 2.** Comparison of (A) conventional powder processing and (B) continuous phase processing of a bimetallic oxide using liquid precursors.



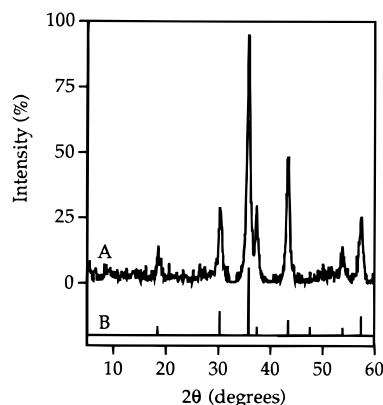
**Figure 3.** X-ray diffraction pattern of the powder prepared from firing of Ni(MEEA)<sub>2</sub>-coated Fe<sub>2</sub>O<sub>3</sub> powders.

A hematite powder was added to sufficient Ni(MEEA)<sub>2</sub> to yield stoichiometric NiFe<sub>2</sub>O<sub>4</sub>. The mixture was stirred using a glass rod until a homogeneous suspension was obtained. It was then fired at 500 °C in order to convert the liquid metal carboxylate to nickel oxide. The X-ray powder diffraction (XRD) of the resulting black powder indicated the presence of both Fe<sub>2</sub>O<sub>3</sub> and NiO (Figure 3). The latter phase had a small crystallite size, estimated to be 23 nm from the broadness of its X-ray reflections. Scanning electron microscopy (SEM) indicated that the features of this powder was little different from those of the Fe<sub>2</sub>O<sub>3</sub> starting materials (Figure 4), implying a homogeneous coating of NiO. Possibly, the homogeneity of the coating is contributed to by partial volatilization of Ni(MEEA)<sub>2</sub> followed by chemical vapor deposition of NiO onto the iron oxide particles.

Upon heating to 800 °C, a reaction occurs between the NiO coating and the Fe<sub>2</sub>O<sub>3</sub> to give nickel ferrite. The XRD pattern of a bulk sample heated to 800 °C indicated that the material had been completely converted to trevorite, NiFe<sub>2</sub>O<sub>4</sub> (Figure 5). Surprisingly, the crystallite size of the product was quite small and was determined to be less than 18 nm from broadening of the X-ray reflections. Scanning electron microscopy of the powder showed that the reason for this was that the reaction of the primary particles of the iron oxide with their nickel oxide coating resulted in a rather startling transformation of the initial particles into a porous solid composed of many very small particles (Figure 4C). It has previously been reported that the formation of ZnFe<sub>2</sub>O<sub>4</sub> via the solid-state reaction of ZnO and Fe<sub>2</sub>O<sub>3</sub> occurs via initial formation of ZnFe<sub>2</sub>O<sub>4</sub> at the interface followed by diffusion of Fe<sub>2</sub>O<sub>3</sub> through the ZnFe<sub>2</sub>O<sub>4</sub> to the ZnO, where further reaction occurs to produce additional ZnFe<sub>2</sub>O<sub>4</sub>.<sup>26</sup> The involvement of such



**Figure 4.** Scanning electron micrographs of (A) Fe<sub>2</sub>O<sub>3</sub> powder, (B) Fe<sub>2</sub>O<sub>3</sub> powder coated with Ni(MEEA)<sub>2</sub> and heated to 500 °C, and (C) Fe<sub>2</sub>O<sub>3</sub> powder coated with Ni(MEEA)<sub>2</sub> and heated to 800 °C.

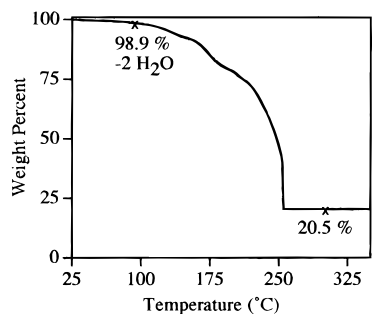


**Figure 5.** (A) X-ray diffraction pattern of NiFe<sub>2</sub>O<sub>4</sub> produced by heating NiO-coated Fe<sub>2</sub>O<sub>3</sub> to 800 °C and (B) a library pattern for NiFe<sub>2</sub>O<sub>4</sub> (JCPDS file 10-0325).

a mechanism in the reaction of the Fe<sub>2</sub>O<sub>3</sub> particles with the NiO coating would account for the “puffing” of the initial chunklike particles into the resulting aggregations that resemble broccoli florets.

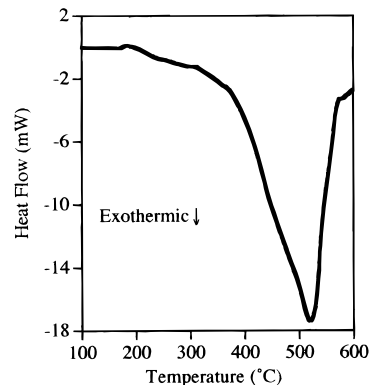
In principle, the most homogeneous starting point for a reaction is as a solution. The difficulty of removing sodium chloride from Fe(MEEA)<sub>3</sub> prepared from FeCl<sub>3</sub>·(H<sub>2</sub>O)<sub>6</sub> and NaMEEA suggests that the liquid metal carboxylates are good solvents for other metal salts. Therefore a 0.5 molar equivalent of Ni(NO<sub>3</sub>)<sub>2</sub> was dissolved in Fe<sub>3</sub>O(MEEA)<sub>7</sub>·5.5H<sub>2</sub>O to prepare a liquid precursor for nickel ferrite. The nickel salt dissolved readily with gently heating to afford a brownish-red solution. Drying in vacuo at room temperature yielded a reddish-brown liquid that elemental analysis indicated

(26) Hopkins, D. W. *J. Electrochem. Soc.* **1949**, *96*, 195.



**Figure 6.** Thermogravimetric analysis trace for  $[\text{Fe}_3\text{O}(\text{MEEA})_7]\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

to contain very little water. The formula of this liquid nickel ferrite precursor may be written as  $[\text{Fe}_3\text{O}(\text{MEEA})_7][\text{Ni}(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$ . Apparently, the coordination of the nickel ions by the MEEA ligands (possibly through chelation by the ether oxygen atoms) is strong enough that the waters of hydration are readily displaced. Thermal gravimetric analysis of this mixture indicated that the material dehydrated at 125 °C and then the organic and nitrate ions burned out over the range 150–330 °C (Figure 6). The XRD pattern of the material from bulk pyrolysis of the precursor at this temperature shows that it is amorphous. However, differential scanning calorimetry (Figure 7) indicates that an exothermic reaction of this powder occurs with an onset temperature of 374 °C and an energy change of  $-126.1$  kJ/mol of  $\text{NiFe}_2\text{O}_4$ . This endotherm can be attributed to crystallization of the amorphous solid to yield nickel ferrite since the XRD pattern of a sample heated to 400 °C demonstrated that well-crystalline phase-pure nickel ferrite was formed. Aside from hy-



**Figure 7.** Differential scanning calorimetry trace for the amorphous  $\text{NiFe}_2\text{O}_4$  phase.

drothermal synthesis, this is the lowest temperature synthesis of nickel ferrite of which we are aware.

### Conclusions

Nickel and iron salts of 2-[2-(2-methoxyethoxy)ethoxy]-acetate are room temperature liquids that have significant potential for the synthesis of ceramic powders by a variety of processes. They may be used to prepare nickel ferrite by a modified powder process, or a liquid precursor may be prepared by dissolution of nickel nitrate into the liquid iron carboxylate. The latter preceramic is not only amenable to processing into different morphologies due to its liquid nature but it converts to nickel ferrite at the low temperature of 400 °C. Furthermore, it is possible to produce a metastable amorphous nickel ferrite from this precursor.

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