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A convenient method for the small-scale preparation of some ferrites

R. T. RICHARDSON
Glasgow College of Technology, Cowcaddens Road, Glasgow, UK

The ferromagnetic spinels, $MnFe_2O_4$, $CoFe_2O_4$ and $NiFe_2O_4$, were prepared in small amounts by the thermal decomposition of mixtures of pyridine-1-oxide and pyridine complexes of the corresponding metal nitrates. The thermal decomposition of the chosen complexes proceeds through a liquid stage and this helps to ensure that there is a homogeneous product and that there is rapid formation of the spinel structure when residues are heated between 1000 and 1200° C. Thin layers of these spinels may be obtained by using a solution of the metal complexes in ethan-1,2-diol. X-ray diffraction and visual examination showed that the initial oxide form is a glassy solid and that the lattice order increases with temperature. $CoFe_2O_4$ and $NiFe_2O_4$ formed directly from the glassy state but a 2Fe: 1Mn mixture initially forms Fe_2O_3 and an unidentified manganese oxide. These reacted at 1200° C to form $MnFe_2O_4$.

1. Introduction

Ferromagnetic spinels are manufactured on a large scale by thermal treatment of well-mixed, finely-divided metal oxides. This requires careful ball-milling and pretreatment and is inconvenient for the preparation of small samples and is inappropriate for the investigation of the effects of slight changes in composition. Electrolytic co-precipitation [1], co-precipitation of oxalates [2], spray-drying of mixed sulphate solutions [3] and thermal decomposition of mixed metal acetate complexes [4] have also been used to obtain well-mixed metal oxides. Only the oxalate and acetate techniques are convenient for the preparation of small amounts of samples and both form solids at an early stage in their thermal decomposition. Thermal decomposition of suitable mixtures of metal complexes, where such decompostion proceeds through a liquid phase maintained till a late stage in the process of oxide formation, can be used for the preparation of small homogeneous samples, or for the formation of small zones of ferrite compositions.

Suitable compounds of iron, manganese, nickel and cobalt can be found among the readily prepared pyridine or pyridine-1-oxide complexes of the metal nitrates. With the exception of iron, these can be obtained as pure materials of well-defined composition. With iron, it has not been found feasible to prepare materials of definite stoicheiometry but a suitable iron(III) precursor can be obtained from iron(III) nitrate and pyridine-1-oxide, and the iron content of each batch can be determined analytically. The chosen nitrate complexes are easily prepared as fine crystalline powders and are soluble in a range of organic solvents. Mixtures can be prepared by either grinding together, or dissolving, preweighed components. Alternatively, the complexes can be stored as solutions in ethan-1,2-diol (ethylene glycol) of up to 0.5 molarity and mixtures prepared by mixing measured volumes. A number of other metal ions, e.g. copper(II), zinc(II), cadmium(II) and magnesium(II) can be obtained by similar means.

Conversion to the corresponding mixed metal oxide lattice is brought about by heating a mixture of complexes (or a solution) through a temperature programme determined by thermogravimetry (TG) and X-ray powder diffraction (XRPD). As the complexes contain both oxidizing and reducing groups the initial stages of the decomposition must be carried out at a controlled rate under well-ventilated conditions to avoid defla-

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TABLE I Recommended sources for manganese, iron, cobalt and nickel

Formula	Equivalent weight (g)
$Mn(pyO)_2(NO_3)_2$	369.1
$Fe(pyO)_n(NO_3)_3$	620–910
$Co(H_2O)_2(pyO)_2(NO_3)_2$	409.1
$Ni(H_2O)(py)_2(NO_3)_2$	376.9

pyO = pyridine-1-oxide
py = pyridine
n ≈ 4 to 7

gration. Using the complexes listed in Table I, all organic matter is lost by 500° C.

2. Experimental details

2.1. Preparative methods for metal complexes

The methods used have been adapted from the accepted techniques of preparation of pyridine [5–7] and pyridine-1-oxide [8, 9] complexes. A review of structural and other properties of nitrato complexes has been published [10].

(a) $Mn(pyO)_2(NO_3)_2$: Manganese(II) nitrate is hygroscopic. A convenient starting material is the 50% wt/vol solution obtainable from laboratory suppliers. A suitable quantity of this solution is mixed with butan-1-ol in a distillation flask and about 2.5 molar equivalents of pyridine-1-oxide are added. The solution is heated until all the water has been distilled out. Pale yellow crystals of $Mn(pyO)_2(NO_3)_2$ are obtained on cooling. These are filtered off, washed with butan-1-ol and diethyl ether and dried under vacuum. The material is photosensitive and should be protected from sunlight.

(b) $Fe(pyO)_n(NO_3)_3$: A suitable quantity of $Fe(NO_3)_3 \cdot 9H_2O$ is dissolved in cold butan-1-ol or propan-1-ol and 5 to 10 molar equivalents of pyridine-1-oxide dissolved in the same solvent, are added with stirring. The buff to yellow precipitate formed is filtered off, washed with propan-1-ol and ether and dried under vacuum at room temperature.

(c) $Co(H_2O)_2(pyO)_2(NO_3)_2$: This is prepared as $Co(pyO)_2(NO_3)_2$ by a technique similar to that used for $Mn(pyO)_2(NO_3)_2$ and then converted to the bis(aquo) complex by exposure to atmospheric moisture for a few days. Under normal conditions moisture absorption stops at the bis(aquo) stage.

(d) $Ni(H_2O)_2(py)_2(NO_3)_2$: A suitable quantity of $Ni(NO_3)_2 \cdot 6H_2O$ is dissolved in acetone and an accurately measured two molar equivalents of pyridine added. The solution is evaporated to dryness in a rotary evaporater, redissolved in acetone and re-evaporated to dryness. The residue is washed out of the flask with ether, filtered off and dried under vacuum.

The anhydrous complexes are slightly hygroscopic and should be stored in stoppered bottles. The metal content of the prepared materials can be determined by thermogravimetry or by titration with ethylenediaminetetraacetate ion.

2.2. Thermal and X-ray examination

A Stanton-Redcroft TG 770 thermobalance was used for thermogravimetric studies and for thermal conditioning of samples for X-ray powder diffraction. This instrument has a small water-cooled furnace with a maximum temperature of 1500° C and allows heating rates of up to 50° C per minute. X-ray powder diffraction data were obtained from film exposed in a 360 mm circumference Debey-Scherrer camera using a Phillips PW 1120/90 power supply and an iron target. Samples for XRPD were prepared by rolling lightly crushed material into needles with "balsa cement".

Mixtures of the required metal composition were prepared by accurately weighing gram quantities of prepared and analysed metal complexes and grinding them together in an agate mortar. Melting and general thermal decomposition behaviour was observed on a Reichert hot-bench before thermogravimetric examination. This was carried out using 2 to 3 milligram samples in 6 millimetre diameter platinum crucibles and was used to establish a heating programme which would avoid deflagration of the sample and to determine the temperature at which volatile material ceased to be evolved.

Samples for XRPD were prepared on the thermobalance using 10 to 15 milligram samples and an appropriate programme of heating rates and isothermal periods. Residues were visually examined at × 30 magnification and then transferred from the crucible to a glass plate, lightly ground, mixed with a small amount of balsa cement and rolled into needles with a microscope slide. Suitable samples can be prepared from 1 to 2 milligrams of residue.

Thin films were prepared from solutions of mixtures of metal complexes in ethan-1,2-diol or formdimethylamide spread on microscope slides and heated on a hot-bench. Films for high temperature treatment were prepared on transparent silica plates. Visual examination was carried out using either a Kyowa FM-S2 binocular microscope or a Vickers M55 projection microscope and transmitted light.

3. Results and discussion

Visual examination of the thermal decomposition residues of the manganese, iron, cobalt and nickel complexes showed them to be glassy in nature as originally formed at between 300° C and 400° C. X-ray powder diffraction examination gave blank films indicating a lack of order in these samples. Heating to higher temperatures (between 800° C and 1000° C) gave materials which were visually polycrystalline and gave well-defined X-ray diffraction patterns. The manganese oxide was not unambiguously identified but the others were identified from JCPDS Powder Diffraction Files as Fe_2O_3 [11], Co_3O_4 [12] and NiO [13]. Attempts to prepare the spinels $MnFe_2O_4$, $CoFe_2O_4$ and $NiFe_2O_4$ all initially led to the formation of glasses at temperatures below 500° C. After heating to 550° C both Co:2Fe and Ni:2Fe samples showed broad lines typical of $CoFe_2O_4$ [14] and $NiFe_2O_4$ [15], respectively, indicating that the spinels were forming directly from the glassy state. A Mn:2Fe mixture showed broad lines attributable to Fe_2O_3 after heating to 550° C but no manganese oxide lines were visible.

Examination of these oxide residues at high temperatures showed that the $CoFe_2O_4$ and $NiFe_2O_4$ lines became sharper in the corresponding samples while the Mn:2Fe oxide system showed lines appropriate to Fe_2O_3 and an unidentified manganese oxide. For samples heated in air $MnFe_2O_4$ did not appear to form below 1100° C, but one sample heated in argon to 1000° C showed well-defined $MnFe_2O_4$ lines [16]. Another sample heated in argon to 900° C showed the presence of both Fe_2O_3 and Fe_3O_4, but none of the samples heated in air showed any detectable amount of Fe_3O_4 on examination by X-ray powder diffraction [17]. The observed behaviour of the Mn:2Fe system is in accord with the reported instability below 1000° C of $MnFe_2O_4$ in favour of a mixture of two solid solutions, α-Fe_2O_3 containing Mn_2O_3, and α-Mn_2O_3 containing Fe_2O_3 [2]. The rate of formation of the $MnFe_2O_4$ spinel at 1100° C and 1200° C was studied by heating a Mn:2Fe mixture to 500° C and then placing samples of the residue, of approximately 2 mg weight, in the furnace of the thermobalance at the required temperature. With such small samples rapid thermal equilibration is obtained. A sample heated at 1100° C for 30 minutes gave an X-ray diffraction pattern indicating that the material was mainly composed of $MnFe_2O_4$ although low-intensity lines corresponding to d spacings of 0.267, 0.183 and 0.169 nm indicated the presence of some unconverted manganese and iron oxides. Samples were heated at 1200° C for periods of 1 min, 15 min and 60 min. The sample heated for 1 min showed only traces of $MnFe_2O_4$, the sample heated for 15 min appeared to be composed mainly of $MnFe_2O_4$ but with Fe_2O_3 lines still evident, and the sample heated for 60 min gave a diffraction pattern showing only $MnFe_2O_4$ (see Table II).

Samples of $CoFe_2O_x$ and $NiFe_2O_x$ compositions prepared by heating appropriate mixtures of complexes to 400° C and then heating at 1200° C for 15 minutes gave sharply defined diffraction patterns indicating the formation of $CoFe_2O_4$ and $NiFe_2O_4$, respectively, (see Table III). Samples examined after treatment at 500° C and 800° C gave spinel diffraction patterns but the lines were broad and diffuse.

The absorption spectrum of thin films of the $CoFe_2O_x$ and $NiFe_2O_x$ materials, obtained by heating films of ethan-1,2-diol solutions on microscope slides to approximately 500° C, showed no detectable bands attributable to

TABLE II Observed d-spacings (nm) in $MnFe_2O_x$ compositions heated at 1200° C

d-spacing after 1 minute (nm)	d-spacing after 15 minutes (nm)	d-spacing after 60 minutes (nm)
0.486	0.491	0.486
0.364	0.368	
0.296	0.299	0.296
0.267	0.269	
	0.255	
0.249	0.252	0.253
0.218	0.219	
0.207	0.211	0.209
0.182	0.183	
	0.172	0.171
0.168	0.168	
	0.162	0.161
0.158	0.159	
	0.149	0.149
0.147	0.148	
0.144	0.145	

TABLE III Observed *d*-spacings (nm) in $CoFe_2O_x$ and $NiFe_2O_x$ compositions heated at 1200° C for 15 minutes

d-spacing observed in $CoFe_2O_x$ (nm)	*d*-spacing observed in $NiFe_2O_x$ (nm)
0.483	0.475
0.295	0.292
0.251	0.249
0.240	0.238
0.208	0.206
0.170	0.169
0.160	0.159
0.147	0.146
	0.130
	0.126
	0.124
	0.119

cobalt(II) or nickel(II) in the 800 to 300 nanometre wavelength range. Such films are yellow in colour and give spectra typical of iron(III) compounds having a strong absorption in the ultra-violet part of the spectrum which tails into the visible region.

Although no detailed studies of magnetic properties have yet been made, crucible-prepared Mn:2Fe products show appreciable ferromagnetism after heating to 1100° C for between 1 and 2 minutes, and the Co:2Fe and Ni:2Fe materials show some ferromagnetic response after heating to 500° C and being allowed to cool in a magnetic field. Attempts have been made to determine the domain structure by using the Faraday technique on thin films of $MnFe_2O_4$, $CoFe_2O_4$ and $NiFe_2O_4$ prepared on transparent silica and conditioned for 1 hour at 1200° C but no domain structure was observed. Of these thin films the $CoFe_2O_4$ and $NiFe_2O_4$ remained optically transparent after this treatment, but the $MnFe_2O_4$ became opaque. Film-thickness was not measured but it was apparent that only thin films adhered well to the substrate. Where the film formed was relatively thick it crazed and became detached from the substrate.

Fragments of the glassy form of $CoFe_2O_x$ and $NiFe_2O_x$, which had been heated to approximately 700° C, showed a ferromagnetic response. The electrical and magnetic properties of the continuous thin films have not been studied as yet, but bulk samples prepared in platinum crucibles lose their glassy sheen as the conversion to well-ordered spinel structures proceeds. The maintained transparency of the $CoFe_2O_x$ and $NiFe_2O_x$ films heated to 1200° C may indicate that such samples are not well-ordered and consequently do not have pronounced ferromagnetic properties.

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