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Manganese ferrite synthesized from Mn(II) acetate + hematite freeze-dried powders

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Abstract

Freeze-drying was used to obtain a homogeneous fine powder containing $(CH_3COO)_2Mn\cdot 2H_2O$ and α-Fe_2O_3 (molar ratio Fe:Mn = 3:1), which was thermally treated for 2 h in N_2 atmosphere, at 400 °C. This composite system was further annealed for 4 h in the same atmosphere, either at 700 °C or at 1000 °C. The 700 °C annealed sample was thermally treated in air at 1200 °C and then rapidly quenched. The phase transformations that occurred in the freeze-dried and heat-treated powders were investigated by thermal analyses, X-ray diffractometry, scanning electron microscopy and Mössbauer spectroscopy. Results showed that MnO–α-Fe_2O_3–Fe_3O_4 compounds were obtained after the first heat-treatment. Samples subsequently annealed in N_2 atmosphere revealed the formation of Fe-rich manganese ferrites and manganowüstite phases. However, a single spinel phase was obtained for the sample that had been annealed and quenched in air.

Keywords: Freeze-drying; Manganese ferrite; Thermal analysis; Mössbauer spectroscopy

1. Introduction

Mn-ferrites ($Mn_{1-x}Fe_{2+x}O_4$) belong to a technologically important group of transition metal ferrites, with many well-known specialised applications such as electronic, microwave and magnetic recording devices. The crystal structure is that of a spinel oxide (space group $Fd3m$) in which the cations occupy tetrahedral (site A) and octahedral (site B) atomic positions in the O^{2-} ions sublattice. When $x = 0$ (i.e., for $MnFe_2O_4$), the cation distribution is usually described by the formula $(Mn^{2+}{}_{1-\delta}Fe^{3+}{}_{\delta})[Mn^{2+}{}_{\delta}Fe^{3+}{}_{2-\delta}]O_4{}^{2-}$, where δ is the degree of inversion in the cation occupancy and the round and square brackets represent sites A and B, respectively [1]. The most common δ value for the partially inverse $MnFe_2O_4$ spinel is 0.2. When $x = 1$ (i.e., for Fe_3O_4), the cation distribution is typical of an inverse spinel, with site A occupied only by trivalent iron and site B half-and-half filled by divalent and trivalent irons.

In commercial technologies where ferrites are used as a rule, materials with high densification are required. Thus, manganese ferrites are often prepared from finely ground and highly reactive precursor powders that, at high temperatures, are densified by sintering through solid-state reactions. Alternatively, several methods of synthesis such as coprecipitation [2,3], reverse micelle [4] or combustion [1], have been tried for the preparation of microcrystalline ferrites. Mn-ferrites were synthesized by the thermal decomposition of oxalates [5] and formates [6] as well. Also, nanocrystalline $MnFe_2O_4$ particles were mechanosynthesized by high-energy ball milling a MnO (manganosite) and α-Fe_2O_3 (hematite) stoichiometric powder mixture [7–9].

In spite of the existence of a variety of methods for Mn-ferrite synthesis, new routes are continuously being investigated in search of novel properties. Current work shows a freeze-drying route for the synthesis of Mn-ferrite from a mixture of powders initially containing $(CH_3COO)_2Mn\cdot 4H_2O$ (manganese(II) acetate tetrahydrate, henceforth termed $MnAc_2\cdot 4H_2O$) and α-Fe_2O_3. The resulting powders obtained by freeze-drying are expected to be chemically more homogeneous, free from contamination by impurities and highly reactive. Freeze-drying was recently used to synthesize copper(II) acetate monohydrate ZnO-matrix composite powders, employed to produce Cu-doped ZnO-based ceramics [10–14].

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Further, the choice of this route was based on the fact that $MnAc_2·4H_2O$ is a salt which is both soluble in water [15] and easily freeze-dried [16]. In addition, studies of the non-isothermal decomposition of $MnAc_2·4H_2O$ using thermogravimetry (TG) [17–20], differential thermal analysis (DTA) [18,19], and differential scanning calorimetry (DSC) [19], in N_2 atmosphere, up to 500 °C, showed that after dehydration followed by thermal decomposition of intermediate compounds [19,21], the final solid product is MnO [17,19,20]. However, in air, a mixture of Mn_3O_4–Mn_2O_3 or solely Mn_2O_3 is formed as residual solid product [17,19–21]. Therefore, under appropriate experimental conditions, Mn-ferrite might be synthesized from the thermal decomposition of precursors initially containing $MnAc_2·4H_2O + \alpha\text{-}Fe_2O_3$, followed by solid-state reactions involving the resulting Mn and Fe-oxides.

Current research studies the thermal decomposition course of the ceramic system based on $MnAc_2·2H_2O + \alpha\text{-}Fe_2O_3$ obtained by freeze-drying and the characterization of solid products after thermal treatments at different temperatures and atmospheres. The thermal, structural and hyperfine properties of the freeze-dried and annealed powders are investigated.

2. Experimental

2.1. Materials, freeze-drying and thermal treatments

A powder mixture of $MnAc_2·4H_2O$ (98.7%, Synth) and $\alpha\text{-}Fe_2O_3$ (99.9%, Carlo Erba), with Fe:Mn molar ratio of 3:1, and also the precursors in separate were processed by freeze-drying.

Initially, the materials were homogeneously diluted in 150 ml of distilled–deionized water, at room temperature. The amount of $MnAc_2·4H_2O$ utilized for the production of the powders was below its solubility limit in water [15] (2.7 mol kg^{-1}), at 25 °C. The aqueous mixture was then slowly frozen inside a glass flask which rotated in contact with a refrigerant fluid (semi-dipped) in a continuous system (Edwards, Shell Freezer) at −50 °C, at atmospheric pressure, for 45 min. Finally, the flask was connected to the freeze-drier which consisted of a vacuum pump (Edwards, E2M2) and a water trap (Edwards, Micromodulyo). During drying stage, the frozen water sublimated under low pressure at 3.2 Pa (2.4×10^{-2} Torr) and was captured in the trap, maintained at −45 °C. All powders were freeze-dried for 24 h.

The freeze-dried mixture was heated under 40 ml min^{-1} nitrogen gas flux, with a heating rate of 5 °C min^{-1}, up to 400 °C, followed by isothermal annealing for 2 h. In a second thermal treatment, part of the sample was heated at a heating rate of 10 °C min^{-1}, followed by an isothermal annealing of 4 h after reaching either 700 °C or 1000 °C. In all cases, the samples' cooling was performed without removing them from the furnace. A final sample was prepared by thermal treatment in air at 1200 °C, followed by rapid quenching in air.

Table 1 schematically describes the conditions for the samples' preparation, labelled as S1, S2, S3, S4 and S31.

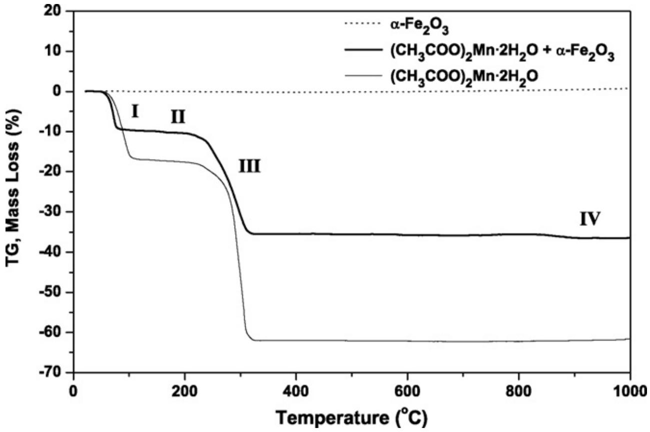

Fig. 1. DSC curves for the $\alpha\text{-}Fe_2O_3$, $MnAc_2·2H_2O + \alpha\text{-}Fe_2O_3$ and $MnAc_2·2H_2O$ freeze-dried powders.

2.2. Thermal, morphological, structural, chemical and Mössbauer characterization

The thermal decomposition course of the resulting freeze-dried powders was analysed by DSC (Shimadzu, DSC-50) on heating up to 500 °C and by TG (Shimadzu, TGA-50) up to 1000 °C. Both DSC and TG were carried out in dynamic N_2 atmosphere (20 ml min^{-1}) with a heating rate of 10 °C min^{-1}, with 6.4 mg of powder, in aluminium and platinum crucibles, respectively.

The morphological aspects of the $MnAc_2·2H_2O + \alpha\text{-}Fe_2O_3$ freeze-dried powders (and of the annealed ones) were analyzed by scanning electron microscopy (SEM) (Shimadzu, SS 550 Superscan) using secondary electrons, following Au-coating. Before characterization by SEM, the heat-treated powders were previously disaggregated in a mortar and passed through a 68-μm sieve.

The $MnAc_2·2H_2O + \alpha\text{-}Fe_2O_3$ freeze-dried powder and the resulting solid products after thermal treatments were characterized by X-ray diffractometry (XRD) (Siemens, D5000), using Cu Kα radiation (λ = 0.154056 nm). The X-ray diffraction measurements were performed in the 2θ range of 10–70°. Chemical analyses of samples, heat-treated at 400 and 700 °C, were obtained by atomic absorption spectrometry (Varian, SpectrA-10 plus).

The ^{57}Fe Mössbauer spectra were carried out using a conventional constant acceleration spectrometer, at room temperature. The γ-ray source was ^{57}Co in Rh-matrix. Powder samples with about 10 mg cm^{-2} of Fe have been used as absorbers and calibration was made by an α-Fe foil spectrum at room temperature.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows DSC curves for the $\alpha\text{-}Fe_2O_3$, $MnAc_2·2H_2O$ and $MnAc_2·2H_2O + \alpha\text{-}Fe_2O_3$ freeze-dried powders.

Table 1
Preparatory conditions of samples

Sample		
S1	Freeze-dried $MnAc_2·2H_2O + \alpha\text{-}Fe_2O_3$	
S2	S1 → 400 °C/2 h in N_2 atmosphere[a]	Slow quenching by switching off the furnace
S3	S1 → 400 °C/2 h → 700 °C/4 h in N_2 atmosphere[a]	
S4	S1 → 400 °C/2 h → 1000 °C/4 h in N_2 atmosphere[a]	
S31	S3 → 1200 °C/2 h in air[a]	Rapid quenching in air

[a] Heat treatment.