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Redox stability and electrical conductivity of $Fe_{2.3}Mg_{0.7}O_{4\pm\delta}$ spinel prepared by mechanochemical activation

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Abstract

This paper addresses the potential of mechanochemical activation of MgO and α-Fe_2O_3 precursor powders to obtain $Fe_{2.3}Mg_{0.7}O_4$ ceramics with enhanced redox stability and electrical conductivity. X-ray diffraction (XRD) and Mössbauer spectroscopy suggest the initial formation of the spinel phase after 5 h of high-energy milling in inert gas, but after 10 h of mechanoactivation, the precursor still comprised hematite as a major phase with minor amounts of magnesiowustite as by-product. The activated mixtures can be nearly completely converted to spinel solid solution by heating to 1173 K, whereas single-phase, dense spinel ceramics can be prepared by sintering at 1773 K in inert atmosphere. These ceramics demonstrated redox stability under mildly reducing conditions ($p(O_2) \sim 10$ Pa), as confirmed by XRD, thermogravimetry and electrical measurements. The electrical conductivity of $Fe_{2.3}Mg_{0.7}O_4$ at this oxygen partial pressure is lower compared to magnetite, but it is still as high as 60 S/cm at 1073 K and 15 S/cm at room temperature. Cooling below 1473 K in air results in a drop of conductivity due to segregation of hematite phase at the grain boundaries. However, the phase separation is kinetically stagnated at 1073 K, and, after slight initial degradation, the retained electrical conductivity is more than 3 orders of magnitude higher compared to hematite and $MgFe_2O_4$ spinel.

Keywords: Spinel; Magnetite; Mechanosynthesis; Electrical conductivity; Mössbauer spectroscopy

1. Introduction

Magnesioferrite $MgFe_2O_4$ with cubic spinel-type structure and its derivatives are of interest for a wide range of applications including magnetic technologies,[1] heterogeneous catalysis and photocatalysis,[2,3] gas and humidity sensing,[4,5] and as sorbent for SO_2 removal[6] and pigments.[7] Recently, magnesioferrites and related spinels attracted attention as promising consumable anode materials for molten oxide electrolysis as an alternative low-CO_2 technology for steel production.[8] Although pure magnetite, Fe_3O_4, may be considered as preferable material for this application from the point of view of maximum electronic conductivity, additions of magnesium and/or other elements may be required in order to improve redox stability and refractoriness of ceramic anodes.[8,9] Another potential application of magnesioferrites relates to the cathode materials for electrochemical reduction on NO_x at 673–873 K.[10,11] The use of stoichiometric $MgFe_2O_4$ electrodes in electrochemical solid electrolyte cells is however limited due to the low level of electronic conductivity in this material (<10^{-3} S/cm at 873 K).[11]

The electronic transport in ferrospinels is considered to occur via small polaron hopping between Fe^{3+} and Fe^{2+} cations in the octahedral sublattice of the spinel structure.[12–14] Therefore, the level of electronic conductivity is determined mainly by the concentration of Fe^{2+} as minority species and the distribution of cations between tetrahedral and octahedral positions. Undoped stoichiometric magnetite is known to possess inverse spinel structure $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$ (parentheses and square brackets denote tetrahedral and octahedral sublattice, respectively) with identical concentration of Fe^{3+} and Fe^{2+} in the octahedral sublattice and, therefore, optimum conditions for hopping and highest electronic conductivity reported of iron-based spinels. On the other hand, in $MgFe_2O_4$, magnesium cations substitute bivalent iron leading to nearly negligible concentration of Fe^{2+}, and have

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preference for octahedral sites with the inversion parameter x in $(Mg_{1-x}Fe_x)[Mg_xFe_{2-x}]O_4$ varying in the range from 0.90 to 0.72 at 770–1370 K.[15] Thus, decreasing magnesium concentration in $Fe_{3-x}Mg_xO_4$ is needed to increase Fe^{2+} concentration and, therefore, electronic conductivity.

The stability limits imposed by temperature and the oxygen partial pressure ($p(O_2)$) on this type of materials are, however, relatively narrow. Magnetite, for instance, is thermodynamically unstable in air below 1667 K and in inert gas ($p(O_2) \approx 10$ Pa) below 1300–1373 K.[16] Phase diagrams predict single-phase domain for $Fe_{3-x}Mg_xO_4$ system in air at $\leq$1073 K only for $x = 1$.[17] On the other hand, stabilization of spinel phase down to low temperatures in atmospheric air was reported for $Fe_{3-x}Mg_xO_4$ ($x = 0.90$–0.95) obtained by combustion synthesis.[9] Still, spinels with decreasing magnesium content ($x < 1$) are expected to be stable at temperatures below 1773 K only within a range of increasingly reducing conditions defining phase boundaries outside which either hematite or magnesiowustite tends to precipitate.[17] Thus, the delicate interplay between magnesium content, temperature and oxygen activity imposes a tight control over the processing conditions of $Fe_{3-x}Mg_xO_4$ spinels, from the powder fabrication to the high temperature sintering, and also determines the range of conditions where the materials can operate.

High-energy mechanochemical treatment is a convenient and simple route for the synthesis of nanocrystalline or amorphous materials at room temperature. It has been used for preparation of spinel powders with enhanced chemical reactivity and non-equilibrium cation distributions.[18] The present work is focused on the evaluation of the potential of mechanochemical activation of precursor powders to obtain $Fe_{2.3}Mg_{0.7}O_4$ ceramics with enhanced redox stability (or meta-stability) and electrical conductivity, by comparison with ceramics obtained by a high-temperature synthesis method (glycine–nitrate combustion technique). The phase evolution during mechanoactivation and subsequent thermal treatment was monitored by X-ray diffraction and Mössbauer spectroscopy, and correlated with the phase stability and electrical conductivity of ceramics in mildly reducing (inert gas) and oxidizing (air) atmospheres.

2. Experimental

The precursors for fabrication of $Fe_{2.3}Mg_{0.7}O_{4\pm\delta}$ ceramics were prepared by two different techniques, including a mechanochemical method, hereafter referred to as mechanical activation (MA), and a glycine–nitrate process (GNP). The MA of MgO (mesh 325, 99+%, Sigma Aldrich) and Fe_2O_3 (<5 μm, ≥99%, Sigma Aldrich) mixtures in molar ratio $MgO:Fe_2O_3 = 0.70:1.15$ was carried out in a Retsch PM 100 planetary ball mill with the planetary rotation of 650 rpm and the vial rotating at 1300 rpm in the opposite direction. Powders mixture (7 g) was placed in a stainless steel vial (internal volume 250 mL) together with balls of the same material (ball to powder mass ratio of 10:1). After closing the vial, the internal volume was flushed with N_2 through a Schrader valve on the cover, with the built in overpressure being released through a second outlet valve. Overheating was avoided by milling for periods of 3 min with intermediate 3 min pauses. Phase formation during the milling was assessed by collecting aliquots of the powder at discrete increasing milling times and analysing those by X-ray diffraction (XRD). The vial volume was flushed with N_2 after each of such interruptions.

The second method, GNP, is a self-combustion technique which uses metal nitrates as oxidant and glycine as a fuel and chelating agent.[19] In the course of GNP, iron nitrate nonahydrate (≥98%, Sigma Aldrich), magnesium nitrate hexahydrate (99%, Avocado Research Chemicals) and glycine (≥99%, SAFC) were dissolved in distilled water and stirred for several hours. Glycine/nitrate molar ratio was 2/1 with respect to stoichiometric reaction assuming that the only gaseous products of reaction are H_2O, N_2 and CO_2. Then, the solution was heated on a hot plate until evaporation of water and subsequent auto-ignition. The foam-like combustion product was ground and annealed in air at 1273 K for 2 h in order to remove organic residues.

Ceramic samples were obtained by pressing the powders 300–400 MPa and sintering at 1673–1823 K for 5–10 h in air or argon flow. The oxygen partial pressure (~10 Pa) in the argon flow was monitored using yttria-stabilized zirconia (YSZ) oxygen sensor. A reference Fe_3O_4 ceramic sample was also prepared by sintering a Fe_2O_3 powder compact in argon atmosphere at 1623 K for 3 h. The fabrication conditions and density of prepared ceramics are summarized in Table 1.

Room-temperature XRD patterns of powdered ceramics were recorded using a Rigaku D/MAX-B diffractometer (CuK_α, $2\Theta = 10$–80°, step 0.02°). Variable-temperature XRD data were collected with a X'Pert MPD Philips diffractometer (CuK_α, $2\Theta = 20$–80°, step 0.03°) equipped with a high-temperature chamber Anton-Parr GmbH HTK16 (Pt heating filament, Pt–Pt/10%Rh thermocouple). Thermogravimetric analysis (TGA, Setaram SetSys 16/18 instrument, sensitivity 0.4 μg, initial samples weight 0.6–0.9 g) was performed in a flow of dried air or argon at 298–1373 K with constant heating/cooling rate of 2 K/min, or on temperature cycling at 973–1373 K with a step of 50 K and equilibration at every temperature for 3 h. In order to determine the absolute oxygen content, the samples were reduced to MgO and metallic iron in a flow of dry 10%H_2–90%N_2 mixture at 1373–1473 K for 45 h. Mössbauer spectra were collected at room temperature in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ^{57}Co source in a Rh matrix. The velocity scale was calibrated using α-Fe foil. The absorbers were obtained by pressing the powdered samples (5 mg of natural Fe/cm^2) into perspex holders. The spectra were fitted to Lorentzian lines using a non-linear least-squares method[20]; isomer shifts (IS, Table 2) are given relative to metallic α-Fe at room temperature. The relative areas and line widths of each peak in a quadrupole doublet and of peaks 1–6, 2–5 and 3–4 in each magnetic sextet were constrained to remain equal during the refinement procedure, assuming samples with no texture effects. Distributions of magnetic splittings were fitted according to the histogram method.[21] The electrical conductivity was measured by AC impedance spectroscopy (Agilent HP4284A precision LCR meter) and 4-probe DC technique using bar-shaped ceramic samples. The measurements were performed