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Chitosan templated synthesis of strontium–iron–oxygen nanocrystalline system

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Abstract

A mixture of ferrites phases containing strontium ortho/hexagonal ferrites was synthesized using chitosan as template and heat treatments. The analysis by XRD, FTIR, SEM, TEM and HRTEM showed the coexistence of the perovskite-like $SrFeO_{2.9}$ and hexaferrite $SrFe_{12}O_{19}$ phases. The ferrites consisted of hard agglomerates containing nanoparticles. The crystallites sizes range between 5 and 20 nm of different morphologies. A possible phase transition model is suggested.

Keywords: A. Precursors: organic; B. Electron microscopy; D. Ferrites; D. Perovskites

1. Introduction

A ferrite is a type of ferrimagnetic ceramic compound, composed of iron oxide (Fe_2O_3) combined chemically with one or more additional metallic elements. According to the crystal structure, the ferrites are divided into four groups namely spinel, garnet, ortho and hexagonal ferrites. These are distinguished by the molar ratio of Fe_2O_3 to a second metal oxide present in the ceramic. In this regard, the spinel has a 1:1 relation Fe_2O_3–MeO, where MeO is a transition metal oxide. In garnet it is $5Fe_2O_3$–$3Me_2O_3$, Me_2O_3 being a rare earth metal oxide. Hexagonal ferrites have $6Fe_2O_3$–1MeO stoichiometry. Finally ortho-ferrites or perovskite-type are characterized by a chemical formula $AFeO_3$ where A corresponds to alkaline-earth or rare earth elements [1–3].

The coexistence of ferrites phases in a given material has been considered before and described as transient phases or undesired by-products of the synthesis reactions. A ternary diagram of Sr–Fe–O system based on information found in the literature has been proposed [4]. In this regard, several aspects to be considered include the Fe/Sr- deficient stoichiometric regions, thermal treatment and oxidant gases [4–6,7–11], among others.

Nevertheless, science and technological applications currently require new properties that rarely can be accomplished by single phase structures. Hence, there is a growing interest in the development of multiphase ceramics [2,12]. For example, the multiferroic materials present simultaneously ferromagnetism and ferroelectricity. Many multiferroics are composites and heterostructures exhibiting more than one ferroic order parameter. These materials show phase diagrams combining different ferroic orders in separate phases [13,14].

In this sense, non-stoichiometric strontium ortho-ferrite $SrFeO_x$ ($2.5 \leq x \leq 3$) is of interest in materials science. This mixed oxide alone or doped with other elements exhibits substantial electronic and ionic conductivities. It is considered a promising material for applications, such as electrodes for solid oxide fuel cells and

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dense ceramic membranes for oxygen separation and partial oxidation of light hydrocarbons [10,15–18].

Furthermore, strontium hexaferrite $SrFe_{12}O_{19}$ is an important hard magnetic material due to its low price, excellent chemical stability, high coercivity, electrical resistivity and magnetic performances. Other applications are memory storage, magnetic recording media, microwave devices and multiferroic materials [19–22].

The appearance of mixture of $SrFeO_x$ and $SrFe_{12}O_{19}$ phases was reported in the preparation of composites based on $SrO–Fe_2O_3–Al_2O_3–B_2O_3$ by glass crystallization method [23]. In this, the starting powders were melted at 1400 °C and cooled by quenching in water to form the glass. Posteriorly, the solids were treated thermally from 600 to 900 °C to produce the glass–ceramics. Their results, related to ferrites phases indicated a dependence of the type of crystalline domain with the annealing temperature. Thus, it was obtained the majority of perovskite phase at lower temperatures, and conversely the hexaferrite phase occurred at high annealing temperatures. Similarly, strontium ortho/hexagonal based ferrites were detected from the carbonation reaction of $SrFeO_x$. The size of particles did not significantly change during the annealing with carbon dioxide at 800 °C. Non-stoichiometric perovskite oxide was synthesized earlier by solid state reaction between $SrCO_3$ and Fe_2O_3 at 1200 °C [4]. Although, a meticulous mechanical processing of the reactant mixture was taken into account to improve the chemical homogeneity of mixture, however, the final material consisted of sintered grains microstructure with separated domains of ferrites phases on the order of tens of micrometers. The microstructural homogeneity is essential for obtaining optimized physical properties of the composite materials. Thus, we propose in this work an innovative synthesis method to control the size/shape and homogeneity of this mixture of ferrites.

Recently, it has been reported the use of polysaccharide macromolecules in materials chemistry. In particular, chitosan, a linear copolymer of glucosamine and N-acetyl glucosamine units linked by β-1 → 4bonds. Chitosan is a natural polysaccharide that is derived from chitin, the major component of the exoskeleton of crustaceans. It is readily amenable to further modification due to the presence of amino and hydroxyl functional groups in its molecular structure. Furthermore, due to its cationic character, it can form polyelectrolyte complexes with metals and anionic biomolecules [24–27]. The use of chitosan as template provides a non-surfactant route that is proposed as an inexpensive and environmentally friendly alternative method for synthesis of metal oxide nanoparticles [28–31]. In this context, we report herein for the first time, the use of chitosan as template for the synthesis of a nanocrystalline system based on strontium ortho/hexagonal ferrites. Particular attention is given to the structure and morphology of this Sr–Fe–O system.

2. Experimental

2.1. Synthesis

The synthesis of Sr–Fe–O system was carried out using chitosan as template and as metal precursor salts iron (III) citrate hydrate (98%, Aldrich) and strontium nitrate (99%, Aldrich) following procedures already reported [29,30]. Briefly, chitosan was mixed with 80 mL of CH_3COOH (3%, v/v). Separately, strontium and iron precursor salts were dissolved in distilled water to get a 20 mL solution containing 0.1 M Sr and 0.1 M Fe ions. The aqueous solution with Fe and Sr ions was added to chitosan solution under stirring in a molar ratio monomer to total metal ions of 0.05. This metal–chitosan solution was added dropwise to a NH_4OH solution (50%, v/v). The gel spheres were decanted from NH_4OH solution [27] and dried at ambient temperature for 96 h. Finally, the dried spheres were calcined at 800 °C in air flow for 6 h after heating from room temperature at 2 °C/min.

2.2. Characterization

The powder X-ray diffractograms were recorded on a SIEMENS powder X-ray diffractometer, model D5005 using Cu Kα radiation, $\lambda = 1.54247$ Å, $2\theta = 10–90°$, nickel filter at 30 mA under a voltage of 35 kV with a scanning speed of 2°/min. The phase identification conducted by means of the MATCH! 2 program (version 2.3.3, Build 434), Crystal Impact, coupled with the Release 2011 PDF-2 database.

The infrared spectra of the precursor and the calcined samples were obtained using a FT-IR NICOLET model iS10 spectrometer. Spectra were collected with a resolution of 4 cm^{-1} using 32 scans in the range 4000–400 cm^{-1}. All samples were prepared as KBr pellets.

The morphology and particle size of the dried powders were examined using scanning electron microscopy SEM HITACHI model S-2400. The evaluation by transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2100 microscope with LaB_6 filament (accelerating voltage of 200 kV).

3. Results and discussion

The interactions between Sr and Fe ions and chitosan were confirmed by infrared analyses. Fig. 1 shows the comparative spectra of chitosan and synthesized Sr–Fe precursor and oxide in the frequency range of 400–4000 cm^{-1}. The FT-IR spectra for sample before the calcination exhibited characteristic bands of chitosan: νOH and νNH vibrations centered at 3400 cm^{-1}, C–H vibration of $–CH_2$ ($\nu = 2890\ cm^{-1}$) and $–CH_3$ groups ($\nu = 2930\ cm^{-1}$); $\nu C{=}O$ of acetyl groups in chitosan at 1660 cm^{-1} and vibration of amine group NH_2 ($\nu = 1580\ cm^{-1}$); a band at 1380 cm^{-1} attributed to amide III, νCN–νNH (combination of NH deformation and νCN stretching); and finally, the bands of νC–O centered at 1070 cm^{-1} and asymmetric stretching of C–O–C at 1160 cm^{-1} [32–35].

The intensity of the wide peak at around 3440cm^{-1} corresponding to $–NH_2$ and –OH groups decreased in the metal-precursor, suggesting that these groups take part in the complexation (Fig. 1B). Small displacement and intensity changes were significant for the bands at 1660 cm^{-1} and 1580 cm^{-1} due to interactions between the metal ions with acetamide and free amine chitosan groups respectively [36,37]. The Fe^{3+} and Sr^{2+} cations are typical hard Lewis acid and therefore more likely to bind to hard Lewis bases such as amines and hydroxyl groups present in chitosan to form metal–chitosan complex stabilized by