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The effect of cation distribution and heat treatment temperature on the structural, surface, morphological and magnetic properties of $Mn_xCo_{1-x}Fe_2O_4@SiO_2$ nanocomposites

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A B S T R A C T

This paper presents the effect of Mn^{2+} substitution for Co^{2+}, in $CoFe_2O_4$ embedded in SiO_2 matrix, on the structural, surface, morphological and magnetic properties. X-ray diffraction (XRD) and Mössbauer spectroscopy indicate the presence of a nanocrystalline mixed cubic spinel. In all cases, for the nanocomposites (NCs) heat-treated at 200 °C, a single, low crystalline ferrite phase was remarked, while for the other heat-treatment temperatures up to 1200 °C and with increasing Mn content, the secondary phase of α-Fe_2O_3 appears, accompanied also by the secondary phase of SiO_2 at 1200 °C. The Fourier transform infrared (FT-IR) spectroscopy confirms the consumption of starting metallic nitrates, the formation of Co-O, Mn-O, Fe-O bonds in ferrites@SiO_2 matrix. The Mössbauer spectra show the characteristic magnetic patterns of Co and Mn spinels. According to the atomic force microscopy (AFM) analysis, the particle size increases from 15 to 80 nm with the increase of Mn content. The specific surface area varies in the range 150–450 m^2/g due to the substitution of Co^{2+} ion with Mn^{2+} ion and decreases with increasing heat treatment temperature, reaching values below 1 m^2/g at 1200 °C. All NCs have pores within the mesoporous range, with high dispersion of pores' sizes. Furthermore, the release of fine nanoparticles in aqueous environment is facilitated by the powders' mesoporous structure preserved at 200, 500 and 800 °C heat treatment temperatures. The porous network collapse after heat treatment at 1200 °C leads to releasing of bigger nanoparticles, in good agreement with AFM observation. Magnetization, coercivity and anisotropy evolve proportionally with the particle size for the NCs heat-treated at 800 °C (M_S = 18.9–36.3 emu/g; M_R = 3.05–14.1 emu/g, H_C = 31.83–53.2 kA/m, K = 0.378·10^{-3}-1.21·10^{-3} erg/cm^{-1}) and inverse proportionally for those heat-treated at 1200 °C (M_S = 30.7–19.4 emu/g; M_R = 11.60–7.20 emu/g, H_c = 127.3–15.9 kA/m, K = 2.45·10^{-3}-0.19·10^{-3} erg/cm^{-1}). The NCs with high Mn content heat-treated at 1200 °C show superparamagnetic behavior, while those with low Mn content display ferrimagnetic behavior.

1. Introduction

In the field of science and technology, the nanomaterials offer unique, advantageous applications due to their different properties compared to the bulk materials [1–6]. Due to their terrestrial abundance and low toxicity, Fe-based materials have been greatly utilized as catalysts in many organic reactions [7]. Nanoferrites and their composites have attracted considerable attention over the past few decades due to their unique and promising electrical, optical, and magnetic properties [6]. It is well-known that the properties of ferrites depend on various parameters that includes the particle size, ion substitution, synthesis route, heat treatment conditions, *etc.* [2,8].

Cobalt ferrite ($CoFe_2O_4$) is a ferrimagnetic oxide with a cubic inverse spinel structure [9–11] and notable features such as large

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