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Synthesis and characterization of $CuFe_2O_4/CeO_2$ nanocomposites

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ABSTRACT

$CuFe_2O_4/xCeO_2$ ($x = 0$, 1, 5, 10 and 20 wt%) nanocomposites have been prepared by urea–nitrate combustion method. The particle size of the as-prepared $CuFe_2O_4$/5 wt% CeO_2 nanocomposite is 5–10 nm which has been revealed from TEM and HRTEM images. The as-synthesized materials have been sintered at four different temperatures (600, 800, 1000 and 1100 °C) for 5 h. The XRD analysis of the samples reveals that the prepared materials possess tetragonal structure and have the composite behaviour. The 1100 °C sintered samples have further been characterized by FT-IR, UV–vis, SEM, ac electrical conductivity, dielectric constant, loss tangent, and Mössbauer spectra. The SEM images clearly show that CeO_2 grows on the surface of the $CuFe_2O_4$. The electrical properties enumerate the ferrimagnetic behaviour of the synthesized materials. The Mössbauer spectra confirm both the inverse spinel structure of the prepared materials and the Fe^{3+} state of iron ions.

1. Introduction

Synthesis and characterization of nanocomposites have gained prominent interest in recent years due to their tailor-made properties. The term nanocomposite encompasses a variety of distinctly different materials mixed at the nanometric scale with specific applications. Some of the reported types of nanocomposites are magnetic–metal (Fe_3O_4–Au) [1], magnetic–metallic oxide (Zn, Ni Ferrite–NiO) [2], magnetic–polymer ($CoFe_2O_4$–Polypyrolle) [3], magnetic–semiconductors (Fe_3O_4–PbS) [4], magnetic–alloy ($(Ni_{0.5}Zn_{0.5})$ Fe_2O_4–$FeNi_3$) [5], magnetic–zeolite [6], etc. The present study deals with the spinel structure ($CuFe_2O_4$) made as composite with the layered fluorite-type structure (CeO_2) and its characterization. In particular, $CuFe_2O_4$ has unique characteristics when compared with other metallic ferrites because of its Jahn–Teller (Cu^{2+}) ions. The ideal $CuFe_2O_4$ is known to be an inverse spinel, where Cu^{2+} ions occupy octahedral [B] sites and Fe^{3+} ions occupy both tetrahedral (A) and octahedral sites. However, it is widely known that the cation distribution in $CuFe_2O_4$ is a complex function of processing parameters and depends on the preparation method of the material.

Very recently, spinel type ferrites such as $CoFe_2O_4$ [7,8], $NiFe_2O_4$ [9,10], $ZnFe_2O_4$ [11], and $CaFe_2O_4$ [12] have gained a prominent interest in the field of energy storage devices especially negative electrodes in Li-ion batteries. In this regard, we have recently reported on $CuFe_2O_4/SnO_2$ nanocomposite [13] as a potential alternative anode for Li-ion batteries. Subsequently, here we have prepared $CuFe_2O_4/CeO_2$ nanocomposite and characterized the structural, electrical and magnetic properties of the materials. The EXAFS and XANES studies of $CuFe_2O_4/xCeO_2$ ($x = 0$, 5, 20 wt%) nanocomposites have been reported elsewhere [14]. CeO_2 is supposed to be one of the most favorable candidate for the anode material [15,16] in Li-ion batteries when compared with other metal oxides of SnO_2 [17], TiO_2 [18], Fe_2O_3 [19] and NiO [20] due to its unique properties such as large oxygen storage capacity, high thermal stability, facile electrical conductivity, diffusivity and the variable valency of Ce^{3+} and Ce^{4+} [16]. Similarly, the surface modification [21] is an important phenomenon in Li-ion batteries leading to an enhancement of the electrochemical activity of the electrodes. Among the surface-modified functional oxide materials [22,23], CeO_2 has gained enormous interest due to an enhancement of the electrochemical stability of the positive electrodes including $LiMn_2O_4$ [24], $LiCoO_2$ [25] and $LiNi_{0.8}Co_{0.2}O_2$ [26].

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Table 1
The quantity of the reactants for the synthesis of $CuFe_2O_4/xCeO_2$ nanocomposites (for 100 g) and the yields

Sample	Reactants (g)				Yields (%)
	$Cu(NO_3)_2 \cdot 6H_2O$	$Fe(NO_3)_3 \cdot 9H_2O$	$Ce(NO_3)_3 \cdot 6H_2O$	$CO(NH_2)_2$	
$CuFe_2O_4$/1 wt% CeO_2	99.00	332.60	2.52	158.74	88.00
$CuFe_2O_4$/5 wt% CeO_2	95.00	319.29	12.60	153.74	85.00
$CuFe_2O_4$/10 wt% CeO_2	90.00	302.00	25.20	147.85	85.00
$CuFe_2O_4$/20 wt% CeO_2	80.00	268.00	50.54	134.97	87.00

Hence, considering the importance of the surface modified nanocomposites, a detailed preliminary study has been carried out on nanocrystalline $CuFe_2O_4$ with CeO_2 at four different concentrations of 1, 5, 10, 20 wt% prepared by simple combustion method. The structural (XRD, FT-IR, UV–vis spectra), morphological (SEM, TEM, HRTEM, SAED), electrical (ac electrical conductivity, dielectric constant, loss tangent) and magnetic (Mössbauer spectra) properties of the material have also been investigated and reported herein.

2. Experimental

The $CuFe_2O_4/x$ wt% CeO_2 ($x = 0$, 1, 5, 10, 20) nanocomposites were prepared using urea–nitrate combustion method [27]. The stoichiometric quantities of starting materials, viz., $Cu(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ce(NO_3)_3$ and $CO(NH_2)_2$ were dissolved in 100 ml distilled water. The actual quantities of the reactants for the preparation of each nanocomposite (for 100 g) and the yields are given in Table 1. The mixed nitrate–urea solution was heated at 110 °C, with continuous stirring. After the evaporation of excess of water, a highly viscous gel, known as precursor, has been obtained. Subsequently, the gel was ignited at 300 °C to evolve the undesirable gaseous products, which has resulted in the formation of desired product in the form of foamy powder. The presented (Table 1) yields are not exactly correct. Due to the combustion reaction, lot of products are coming out the reaction vessel. So we cannot calculate the exact value. Subsequently, the powder was sintered at different temperatures (600, 800, 1000 and 1100 °C) for 5 h to obtain ultrafine powders of $CuFe_2O_4/CeO_2$ nanocomposites.

The compound formation, phase purity and crystallinity of the ferrite materials were identified by powder X-ray diffraction (XRD) technique using an X-ray diffractometer (PANalytical (Make), X'per PRO (Model), Cu Kα radiation; $\lambda_{Cu} = 1.5405$ Å). The FT-IR spectra of the samples were recorded with the KBr discs in the range of 400–1000 cm^{-1} using a PerkinElmer spectrophotometer (PerkinElmer, UK, Paragon-500 model). Diffuse reflectance spectroscopy measurements were carried out on a Cary Varian 1E spectrometer in the range of 200–800 nm. The particle size was analyzed using TEM (JEOL-JEM 100SX microscope) operating at an accelerating voltage of 200 kV. The morphological features have been analyzed through SEM (JEOL S-3000 Model). The ac conductivity measurements were made at room temperature using impedance analyzer HIOKI 3532 in the frequency range of 42 Hz to 5 MHz. The room-temperature Mössbauer measurements were made in transmission geometry using a conventional spectrometer in a constant acceleration mode. A ^{57}Co/Rh γ-ray source was used. The velocity scale was calibrated relative to ^{57}Fe in Rh. A proportional counter was used to detect the transmitted γ-rays. Mössbauer spectral analysis software RECOIL [28] was used for the quantitative evaluation of the spectra. The degree of inversion (λ) was calculated from the Mössbauer subspectral areas ($I_{(A)}/I_{[B]} = (f_{(A)}/f_{[B]})\lambda/(2-\lambda)$) assuming that the ratio of the recoilless fractions is $f_{(A)}/f_{[B]} = 1$. Here, the degree of inversion is defined as a fraction of the tetrahedral (A) sites occupied by iron cations; i.e., the structural formula of copper ferrite may be written as $(Cu_{1-\lambda}Fe_{\lambda})[Cu_{\lambda}Fe_{2-\lambda}]O_4$, where round and square brackets denote sites of tetrahedral (A) and octahedral [B] coordination, respectively.

3. Results and discussion

3.1. Structural studies

The XRD patterns of as-prepared $CuFe_2O_4/x$ wt% CeO_2 nanocomposites and thermally treated at different temperatures (600, 800, 1000 and 1100 °C) are shown in Fig. 1. The as-prepared (Fig. 1a) sample contains broad diffraction peaks corresponding to $CuFe_2O_4$ along with the presence of CuO and Fe_2O_3 phases. The observed broad peaks indicate the nanocrystalline nature of the as-synthesized materials as well as the amorphous behaviour of the materials. When the sintering temperature increases to 600 °C, large number of peaks emerged that correspond to impurity phases of precursor. In order to avoid the impurity phases, the samples were further sintered at 800 °C. As expected, the XRD pattern reveals the formation of only $CuFe_2O_4$ compound with the lattice planes of (2 0 2), (2 2 0), (3 1 0), (3 1 1), (2 2 2), (4 0 0), (0 0 4), etc. [14]. Samples sintered at higher temperatures of 1000 and 1100 °C exhibit very sharp and well-defined peaks confirming the increased crystallinity of the compounds. Unfortunately, no peak for CeO_2 is identified, which infers that the added CeO_2 is dissolved in the spinel structure of $CuFe_2O_4$ [23] or otherwise it coated on the surface of the $CuFe_2O_4$ particles [22]. Generally, the Bragg planes of (4 2 2) and (4 4 0) correspond to tetrahedral and octahedral sites of spinel type materials, respectively [29]. For $CuFe_2O_4$/1 wt% CeO_2 sample, the relative intensity of the XRD peak corresponding to the (4 4 0) plane, I_{440}, increases from 6.82 to 9.47 compared with the parent $CuFe_2O_4$ [28]. This indicates that the added Ce^{4+} ions enter into the octahedral [B] sites causing the replacement of some of the Fe^{3+} ions from [B]-sites into (A)-sites. As a consequence, the relative intensity of the XRD peak corresponding to the (4 2 2) plane I_{422}, increases from 6.51 to 8.14. Thus, it can be concluded that the added Ce^{4+} ions enter into the B-sites of copper ferrite. The calculated lattice constant values (Table 2) enumerate that the samples possess tetragonal structure and the values slightly increase with the addition of CeO_2, which may be due to the difference in ionic radii of Ce^{4+} and Fe^{3+} ($r(Ce^{4+}) = 0.87$ Å, $r(Fe^{3+}) = 0.645$ Å). The primary particle size calculated using Debye–Scherrer formula (Table 2) indicates the growth of particles with increasing temperature.

The XRD patterns of $CuFe_2O_4$/5, 10 and 20 wt% CeO_2 nanocomposites sintered at different temperatures are shown in Fig. 1b,c and d. It is observed that the intensity of CeO_2 peaks, i.e., (1 1 1) at 28° and (3 1 1) at 56.7°, in all the samples increases with increase in CeO_2 wt% as well as with sintering temperature. A scrutiny of the lattice parameter values of c and a makes it clear the retention of tetragonal structure all along. It is understood that the tetragonal structure of parent $CuFe_2O_4$ remains more or less intact. Thus, addition of CeO_2 does not have much influence on the original structure of $CuFe_2O_4$, and hence it is presumed that a composite has been resulted. The calculated primary particle size of the materials decreases with increasing concentration of CeO_2 (see Table 2), which is due to the formation of secondary phases that hinders the grain growth of the primary particles [30].

FT-IR spectra of 1100 °C sintered $CuFe_2O_4/xCeO_2$ ($x = 0$, 1, 5, 10, 20 wt%) nanocomposites are shown in Fig. 2. In ferrite the metal cations are situated in two different sub-lattices namely tetrahedral (A-sites) and octahedral (B-sites) according to the geometric configuration of the oxygen ion nearest neighbours. The band υ_1 around 600 cm^{-1} is attributed to stretching vibration of tetrahedral complexes and υ_2 around 400 cm^{-1} to that of octahedral complexes. It can be seen that the observed band at 570 cm^{-1} in the spectrum of $CuFe_2O_4$ is attributed to the stretching vibration of tetrahedrally coordinated Fe^{3+}—O^{2-} bonds. The similar spectral features are also observed for all composites irrespective of the amount of added CeO_2. At higher concentration of CeO_2 ($\geq$10 wt%), a small band is noticed around 650 cm^{-1}, which is due to the Ce–O vibration [31].

Fig. 3 shows the UV–vis spectra of $CuFe_2O_4$ sample and of $CuFe_2O_4/xCeO_2$ ($x = 0$, 1, 5, 10, 20 wt%) nanocomposites sintered at