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Novel magnetodielectric cobalt ferrite–titania–silica ceramic composites with tunable dielectric properties

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ABSTRACT

The cobalt ferrite (CF)–titania (TiO_2)–silica (SiO_2) system has been studied to produce new ceramic composites by conventional solid state reaction. The microstructure of the sintered CF–TiO_2–SiO_2 mixture has been related to compositional modifications in terms of SiO_2/TiO_2 weight ratio keeping constant the CF weight percentage. Microstructural characterization of the sintered bodies was performed in order to understand microstructure evolution, and to quantify the phases volume fraction. The final compositions after sintering differ significantly from the starting ones as a consequence of the reaction of titania with the ferrite, and the formation of the ilmenite-type $CoTiO_3$. Four different distributed phases are present, depending on the starting SiO_2/TiO_2 weight ratio. The complex permittivity dispersion of ceramic composites was investigated and correlated to their microstructure. Lastly, CF-SiO_2 magneto-dielectric composites are suggested as possible candidates for high frequency applications as miniaturized antennas.

1. Introduction

Nowadays heterostructured oxides are receiving increasing attention as they often allow new applications in electronic to be developed, catalysis and biomedical field. To that end a growing effort is aimed at the development of new structures featuring combinations of magnetic, dielectric, ferroelectric, photocatalytic materials, in order to improve properties [1–4]. Many such heterostructures are based on spinel ferrites and/or titanium compounds, which are selected as starting hub of the material design for a given application. Spinel CF, due to its high coercivity, large magnetostriction, chemical stability [5], photomagnetic and antibacterial properties [6,7], is a good candidate for use in heterostructures in a whole range of applications. For example, heterostructures of CF were developed with: multi-walled carbon nanotubes for the removal of uranium (VI) ions from aqueous solution [8]; titania and silica as magnetic photocatalyst [9] for gene/enzyme delivery [10], and bioseparation/purification of nuclei acids [11]; ferroelectric titanates for magnetoelectric memory devices, transducers; etc. [12,13]. Amorphous silica is often used as a coating to improve the chemical stability of the CF and its biological affinity [14,15], or to prevent electron donation at the CF/titania interface [16]. Silica does not directly influence the magnetic and dielectric properties of the bulk CF due to its smaller dielectric constant and non-magnetic nature [17] – even though silica-mediated interparticle spacing can modulate the collective behavior of magnetic nanoparticles and so their magnetic surface anisotropy [18,19]. On the other hand, silica can influence the overall macroscopic properties of the composite, and CF can react with titanium compounds when heat-treated at high temperatures [20]. Titania is attractive for its high static dielectric constant and refractive index, incipient ferroelectricity and low-loss dielectric properties [21,22], and it is generally used together with magnetic particles in the photocatalytic detoxification of wastewater [23,24]. The reactivity of CF-TiO_2 mixtures can lead to different in situ composites, which can be regarded as a useful, preliminary approach in the search of novel multifunctional materials for many applications [20,25]. Titanium-based oxides including metals, such as cobalt and iron are known as inorganic functional materials with wide applications in different fields [26]. In particular $CoTiO_3$ (CT) with ilmenite structure in the rhombohedral system is important for chemical and electrical applications due to its weak magnetism and semiconductivity [27–29], which allow potential applications such as gas sensors [30], magnetic recorders [31], catalysts [32], and Li-ion batteries [33]. A recent study has shown

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that in situ synthesis of CF/CT-based composites are easily prepared by displacement reaction, starting from TiO_2/CF mixture with a molar ratio smaller than one [20]. Controlling the microstructure through the ceramic process can offer a potential for applications in the areas of high-density data storage, ferrofluids, magnetic resonance imaging, color processing and magnetic refrigeration [34].

In this work, we focused on the preparation and microstructural characterization of ceramic composites obtained starting from CF–TiO_2–SiO_2 powder mixtures. The samples were prepared by the conventional solid-state reaction process, in which the amount of CF was kept constant at 80 wt%, and the SiO_2/TiO_2 mass ratio was gradually increased from zero to one. In this way the effects of SiO_2 and TiO_2/CF molar ratio on the CF-TiO_2 phase equilibria were evaluated. The magneto-dielectric properties were studied between 1 MHz and 2 GHz. Magnetodielectric CF-SiO_2 composites display relative magnetic permeability (μ_r) greater than unit, reasonably low values of relative dielectric permittivity (ϵ_r), thus yielding a favorable miniaturization factor [$n=(\mu_r\,\epsilon_r)^{1/2}$] without affecting the radiating properties, also reducing the amount of energy trapped in the magnetodielectric substrate of miniaturized antennas [25].

2. Materials and methods

Commercial TiO_2 nanopowder (P25, Degussa) was dispersed in distilled water to obtain a suspension at 42.4 wt% solid content. The suspension was acidified to pH 3.6 by adding a suitable amount of HCl 0.01 M, which reduced the solid content to 32.1 wt%. Amorphous silica suspension was prepared by diluting a commercial sol (Ludox HS-40, Grace Davison, USA) in distilled water down to 5 wt% solid content. The two stable suspensions were mixed together in order to get a SiO_2/TiO_2 mass ratio of 1:3 and dried in an oven at 373 K. The residue solid was sieved at 250 μm and mixed in a 3D Turbula apparatus for 15 min. CF powders with $CoFe_2O_4$ nominal composition were synthesized by the mixed oxides route at 1073 K for 4 h [20]. Similarly, CT powders with $CoTiO_3$ nominal composition were synthesized at 953 K for 6 h. The pure crystalline CF powders were mixed with dried TiO_2 powder, SiO_2/TiO_2 powdered mixtures, and dried SiO_2 powder, as shown in Table 1. The sample ID, reported in the first column of Table 1, regards all the acronyms of the starting compound present in the sample (CF=$CoFe_2O_4$, T=TiO_2, S=SiO_2, CT=$CoTiO_3$) while the number represents the mass ratio SiO_2/TiO_2, where both the compounds are present.

All powder mixtures were wet ball-milled, freeze-dried and subjected to cold linear pressing at 100 MPa to produce 12 mm diameter, 2÷3 mm thick disks. Isostatic pressing at 300 MPa was applied to the disks to obtain green homogeneous bodies, which were then sintered in air at 1527 K for 8 h. A constant heating rate of 150 K/h was employed to reach the sintering temperature plateau, and the sintered samples were brought back to room temperature by natural cooling of the furnace. After sintering, the ceramic bodies were ground to remove the surface layers in order to ensure a reliable X-Ray Diffraction analysis (XRD).

Table 1
Starting compositions of the materials.

Sample identification	Starting CF (wt%)	Starting TiO_2 (wt%)	Starting SiO_2 (wt%)	Starting Co_3O_4 (wt%)
CT	0	50	0	50
CFT	80	20	0	0
CFTS-1	80	10	10	0
CFTS-3	80	5	15	0
CFS	80	0	20	0

Phase compositions of the calcined and sintered samples, and their relative phase volumes, were determined by combining XRD analysis, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDXS) data. XRD patterns were obtained at room temperature on a Bruker D8 X-ray diffractometer (θ–θ) using Cu K_α radiation in the range $15° \le 2\theta \le 70°$ at 2.4°/min scanning rate. Relative phase fractions were measured by image analysis of the images of polished sections obtained with a Field Emission Scanning Electron Microscope (FE-SEM) (Sigma, Zeiss) coupled with an Energy Dispersive X-ray Spectrometry (EDXS) probe. The images, at a 1024×768 pixels resolution, were processed off-line using the Image-Pro Analyzer 7.0 software [35]. Assuming a shape factor of the grains and pores of one, i.e. assuming no preferential orientation of the grains of any of the detected phases, the phases were identified, and the volumetric fraction determined as the ratio of the number of pixels attributed to each specific phase to the total number of pixels in the image. The relative density of the sintered samples was calculated as the ratio between the samples' density (determined by Archimedes' method) and the theoretical density estimated from the phases detected by XRD diffractograms and the stoichiometry of the starting powders.

Dielectric characterization in the 1 MHz–2 GHz frequency range was performed with an Agilent 8714ET vector network analyzer coupled with a coaxial line. The dielectric permittivity was calculated from the measured amplitude and phase of the reflected electromagnetic wave. Prior to each measurement, the parallel faces of the cylindrically shaped samples were painted with a silver paste and heated in a furnace for at least 1 h at 260 °C to evaporate the solvent.

3. Results and discussion

CT formation was confirmed by XRD analysis on the same powder mixture after calcination at 953 K for 6 h, the XRD patterns being shown in Fig. 1. In the same figure, the patterns of stoichiometric TiO_2 commercial powders, CFT, CFTS-1, CFTS-3 and CFS powders mixtures are reported as well. The analysis of the CT diffractograms shows that at 953 K the reaction between Co_3O_4 and TiO_2 is not yet completed, the residual TiO_2 being fully converted to rutile. The CT amount (PDF No. 15-866) was estimated to

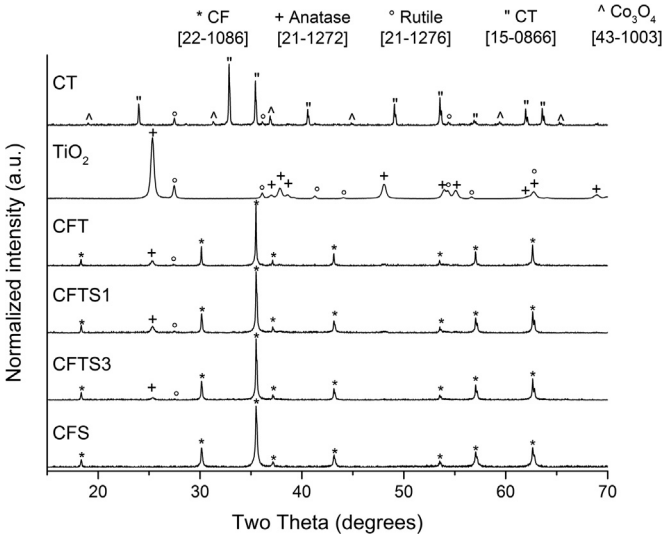

Fig. 1. Normalized XRD patterns of calcined CT powders, commercial TiO_2 nanopowders, and CFT, CFTS-1, CFTS-3 and CFS powders mixtures.

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