Physica B xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Structural and magnetic properties of nanostructured composites $(SrFe_{12}O_{19})_x(CaCu_3Ti_4O_{12})_{1-x}$

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A R T I C L E I N F O

Keywords:
$CaCu_3Ti_4O_{12}$
$SrFe_{12}O_{19}$
Composite
Magnetization
Magnetic resonance

A B S T R A C T

$(SrFe_{12}O_{19})_x(CaCu_3Ti_4O_{12})_{1-x}$ (x = 0.01, 0.03, 0.07, 0.1) composites were synthesized using a solid state method, while the pre-synthesized strontium hexaferrite $SrFe_{12}O_{19}$ (SFO) was added to the stoichiometric amount of CaO, CuO and TiO oxides to form the $CaCu_3Ti_4O_{12}$ (CCTO) structure around SFO microinclusions. The structural and microstructural properties of obtained composites were studied by X-ray diffraction, scanning electron microscopy and transmission electron microscopy techniques. The magnetic properties were studied by electron spin resonance and magnetometry methods. Based on all experimental data we can conclude, that SFO_xCCTO_{1-x} nanostructured composites were formed only for concentrations x = 0.03 and x = 0.07, where SFO nanoinclusions are inside CCTO matrix, that leads to the strong mutual influence of the magnetic properties of both component.

1. Introduction

Composite materials attract much attention due to the possibility to create the new structure combining the components with high values of the magnetic susceptibility and dielectric permittivity in different component proportions, because they can be used in variety of applications. They exhibit unexpected new physical properties, which can depend on the synthesis method and the internal structure of the composite. The ideal dual-phase $(Bi_4Ti_3O_{12})_x(CaCu_3Ti_4O_{12})_{1-x}$ (x = 0–1.0) composite system with separate orthorhombic and cubic phases gives a high dielectric constant ($\varepsilon' > 3000$) at 100 Hz at room temperature for x = 0.8, that makes these composites applicable for the fabrication of miniaturized global positioning system (GPS) patch antennas [1]. The excellent absorption properties of $SrFe_{12}O_{19}$-based materials indicated their great potential as microwave-absorbing materials. So the microwave absorption results for $SrFe_{12}O_{19}$-TiO_2 indicated that the minimum reflection loss for a specimen with 4.2 mm thickness reached up to −33 dB [2]. The reduced graphene oxide/strontium ferrite/polyaniline ternary nanocomposites exhibited the best absorption property (−45.00 dB) at 16.08 GHz with the 5.48 GHz bandwidth with the optimum matching thickness of the sample 1.5 mm [3]. Special attention is paid to the core-shell structured composites. The excellent review about the applications of exchange coupled bi-magnetic hard/soft and soft/hard ferromagnetic core/shell nanoparticles in the field of permanent magnets, recording media, microwave absorption, biomedical applications was published earlier [4].

Here we investigate the magnetic properties of the composite materials which consist of two inorganic components. One of the components is $CaCu_3Ti_4O_{12}$ (CCTO) which has the perovskite-type structure (space group $Im\bar{3}$, a = 7.391 Å) [5,6] and undergoes the phase transition into the antiferromagnetically ordered phase below T_N = 25 K and a Weiss constant of $\Theta_W \sim -30$ K [7]. The dielectric constant of CCTO has a high value $\varepsilon = 10^3 - 10^5$ in a wide temperature range (40–450 K) for frequencies up to 10 MHz [8,9]. As the second component of the composite material besides CCTO we chose the strontium hexaferrite $SrFe_{12}O_{19}$ (SFO) with ferromagnetic properties to modulate the magnetic properties of the composite. The crystal structure of SFO belongs to the space group $P6_3/mmc$ with the cell parameters a = b = 5.89 Å and c = 23.1 Å [10,11], and the temperature

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http://dx.doi.org/10.1016/j.physb.2017.09.095
Received 28 June 2017; Received in revised form 18 September 2017; Accepted 22 September 2017
0921-4526/

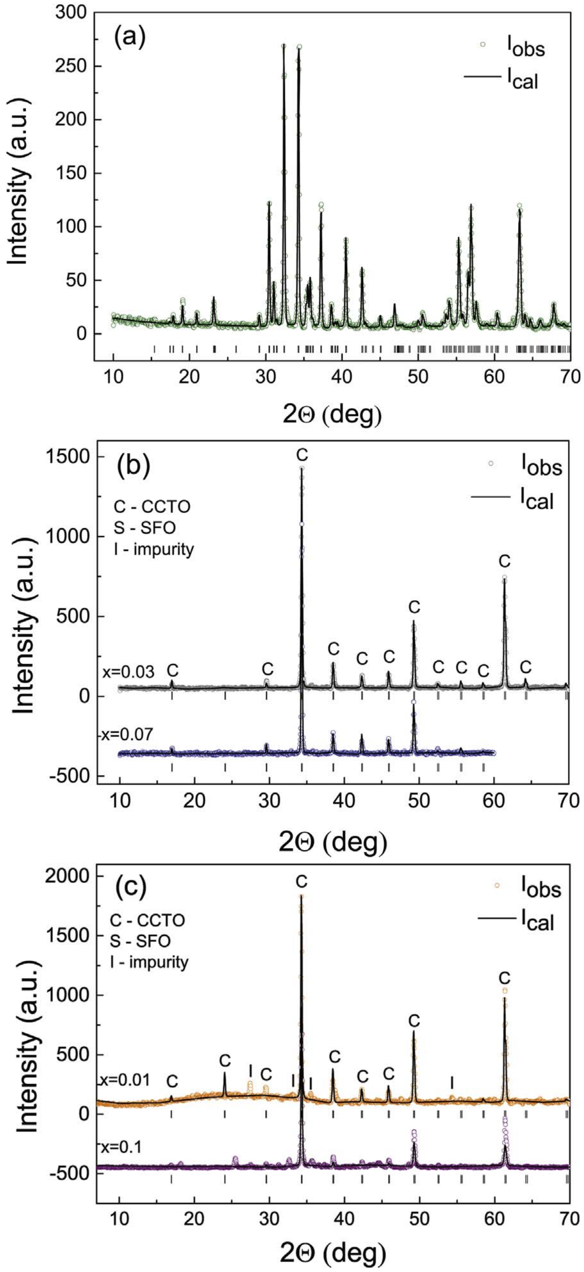

Fig. 1. XRD pattern of: (a) pure SFO; (b) SFO_xCCTO_{1-x} composites for x = 0.03, 0.07; (c) SFO_xCCTO_{1-x} composites for x = 0.01, 0.1.

Table 1
Lattice parameters of SFO_xCCTO_{1-x} ceramic samples.

Sample	Phase	a (Å)	Impurities
x = 0.01	$CaCu_3Ti_{4-y}Fe_yO_{12}$	7.400(1)	TiO_2
x = 0.03	$CaCu_3Ti_4O_{12}$	7.391(1)	–
x = 0.07	$CaCu_3Ti_4O_{12}$	7.392(1)	–
x = 0.1	$CaCu_3Ti_{4-y}Fe_yO_{12}$	7.395(1)	Fe_2O_3, TiO_2, SrO
x = 0[a]	$CaCu_3Ti_4O_{12}$	7.391(1)	–

[a] Data from Ref. [5].

of the phase transition to the ferromagnetic state $T_C \sim 730$ K [12,13].

Here we present the experimental study of $(SrFe_{12}O_{19})_x(CaCu_3Ti_4O_{12})_{1-x}$ (SFO_xCCTO_{1-x}) (x = 0.01, 0.03, 0.07, 0.1) composites prepared according to the specific solid state technology, wherein the pre-synthesized SFO is the nucleus for the formation

Table 2
Average content of the elements in SFO_xCCTO_{1-x} composite obtained by EDS-microanalysis equipped in a SEM.

Sample		Ca	Cu_3	Ti_4	O_{12}	Sr	Fe_{12}	O_{19}
x = 0.01	average value	1	3.02	3.59	14.17	–	8.97	19
	error	0.24	0.49	0.51	1.44	–	5.16	1.44
x = 0.03	average value	1	3.69	4.13	15.31	–	16.38	19
	error	0.06	0.23	0.22	0.47	–	3.56	0.47
x = 0.07	average value	1	3.52	4.11	15.73	–	12.36	19
	error	0.17	0.57	0.59	0.83	–	2.66	0.83
x = 0.1	average value	1	3.92	4.28	13.56	–	8.4	19
	error	0.27	1.06	1.08	2.32	–	3.1	2.32

of CCTO phase. To investigate the mutual influence of the magnetic properties of the composite components on each other we performed the investigations of SFO_xCCTO_{1-x} by electron spin resonance and magnetometry methods and compared these data with pure components.

2. Experimental details

The first step of the creation of composite materials was the synthesis of $SrFe_{12}O_{19}$ (SFO) strontium hexaferrite. SFO was synthesized by the standard solid-phase method. According to this technology the stoichiometric amount of pure $SrCO_3$ and FeO were taken. The obtained mixture was annealed at 1000 °C during 8 h with the intermediate grinding.

SFO_xCCTO_{1-x} composites with x = 0.01, 0.03, 0.07 and 0.1 were prepared also by the conventional solid-state synthesis route. The pre-synthesized strontium hexaferrite was added to the stoichiometric amount of the oxides CaO, CuO and TiO to form the CCTO structure around SFO microinclusions. The resulting mixture was annealed at 1000 °C for 24 h with several intermediate grindings.

The X-ray diffraction studies of the obtained samples were performed on a Shimadzu XRD-7000 S automatic diffractometer with 2 s exposure in point. The microstructure and elemental composition of SFO_xCCTO_{1-x} composites was studied with an EVO 50 XVP scanning electron microscope and energy dispersive x-ray spectroscopy (EDS, Oxford, Inca Energy 350, equipped in a scanning electron microscope). Structural studies by transmission electron microscopy were carried out on a JEOL JEM-2100 high-resolution electron microscope.

Magnetic resonance spectra of composites were measured on an ER 200 SRC (EMX/plus) spectrometer (Bruker) at the frequency of 9.4 GHz with a flow N_2 Temperature Controller RS 232 cryostat (Bruker) in the temperature range from 100 to 300 K. The magnetization was measured on the PPMS-9 device in the temperature range from 10 to 400 K in zero-field-cooled (ZFC) and field-cooled (FC) regimes. The magnetic hysteresis loops were measured in the field range 1 T.

3. Structural and microstructural properties

The structure of SFO and SFO_xCCTO_{1-x} (x = 0.01, 0.03, 0.07, 0.1) was studied with X-ray diffraction (XRD) analysis (Fig. 1). The X-ray diffraction pattern of the pre-synthesized SFO sample is shown in Fig. 1a. The investigated sample was in the single-phase state and impurities were absent. The Rietveld refinement of the SFO X-ray diffraction pattern confirms the $P6_3/mmc$ space group with cell parameters values of a = 5.8751 Å and c = 23.0395 Å.

Each diffraction pattern of SFO_xCCTO_{1-x} contains reflections corresponding CCTO ($Im\bar{3}$ space group [5]) phase. SFO and impurity reflections were not observed in the diffraction patterns of SFO_xCCTO_{1-x} samples for x = 0.03 and x = 0.07 (Fig. 1b), therefore, it can be assumed that there was formed the nanostructured composite with SFO inclusions inside CCTO matrix. If the content of SFO was 1% (x =