

Synthesis and Characterization of a Core-shell Material Using $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and Cobalt Ferrite Nanoparticles

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In this paper we describe the synthesis of a core-shell material using yttrium superconducting ceramic material (YBCO) and cobalt ferrite nanoparticles in order to obtain a nanostructured material with magnetic properties. The advantages of such material aim the selective deposition of nanofilms oriented in magnetic fields. To obtain this core-shell material, the solutions of the nitrates were first obtained by dissolving the salts in demineralised water. The suspension with cobalt ferrite nanoparticles was obtained by co-precipitation method. To obtain $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -coated magnetic nanoparticles by autocombustion reaction the solutions of nitrates and citric acid were used. The ratio of the metal ions: Y:Ba:Cu was 1:2:3, and between the oxidant and the reducing agent was used a citrate / nitrate mass ratio equal with 0.7. The final material was analyzed by X-ray diffraction (XRD), electronic scanning microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), high resolution transmission electron microscopy (HRTEM) and vibrating sample magnetometer (VSM).

Keywords: core-shell material, nanoparticles, ceramic material, cobalt ferrite

High temperature superconducting ceramic materials have many applications and, therefore, the improvement of their properties is a current necessity [1-4].

For improvement the properties of high temperature superconducting materials have been approached, such as the substitution of some atoms [5], the introduction of some damaged areas by irradiation with ions or neutrons [6, 7], addition of secondary phases [8, 9] etc. The addition of SiC nanoparticles had a positive effect on critical current density [10].

The addition of magnetic nanoparticles has been aimed for improving the magnetic properties of high temperature superconductors [11, 12].

Until recently it was believed that superconductivity and magnetism are reciprocally exclusive, since superconductivity disappears by applying an external magnetic field. Recently, it has been shown that these two properties can coexist when the material is in nanocrystalline form [13].

Core-shell materials could be synthesized by several methods depending on the nature of the component materials and their applications. Compared to simple nanoparticles, core shell materials have more practical applications [14, 15]. They can be used for controlled drug delivery [16], medical imaging [17], catalysis [18, 19], electronics [20].

In this paper we describe the synthesis of a core-shell material using cobalt ferrite nanoparticles and the YBCO high temperature superconductor. The advantages of such a material are to obtain magnetic field-oriented nanofilms.

Experimental part

All reagents used for synthesis were analytical grade, as commercial products; they all were purchased from

Merk. To obtain the core-shell material, the solutions of the nitrates were first obtained by dissolving the salts in demineralised water.

The suspension of cobalt ferrite nanoparticles was obtained by the co-precipitation method using stoichiometric amount of Co^{2+} and Fe^{3+} , and the molar ratio $\text{Co}^{2+}/\text{Fe}^{3+}$ between metal ions was 2:1.

In order to obtain YBCO-coated magnetic nanoparticles by autocombustion reaction solutions of nitrates and citric acid were used. The ratio between the metal ions: Y:Ba:Cu was 1:2:3, and between the oxidant and the reducing agent a molar ratio of 0.7 was used. The solutions obtained were mixed and the final mixture was heated on the hob to obtain the precursor gel, which dehydrates to obtain a porous material. This was heated at 900 °C for one hour.

The flow chart of the process for obtaining the composite material YBCO/cobalt ferrite nanoparticles is as follows (fig. 1).

X-ray diffraction was carried out on a PANalytical Empyrean equipment which uses Cu_α radiation (1.541874), equipped with programmable divergence slit on the incidence side and a programmable anti-scatter slit mounted on PIXcel3D detector on the diffracted side. The scan was done by using Bragg Brentano geometry with a step size of 0.02° and a counting time per step of 100 s in the range of $2\theta = 20-70$.

Scanning electron microscope (SEM) QUANTA INSPECT F field emission gun resolution 1.2 nm was used to observe the sample surface morphology, and using energy dispersive X-ray (EDX) with the resolution to MnK_α 133 eV, elemental distribution in the powder was determined.

TEM analyses were performed on a Tecnai G2 F30 S-TWIN high-resolution transmission electron microscope (HR-TEM) equipped with energy dispersive spectroscopy (EDS) as well as a selected area electron diffraction

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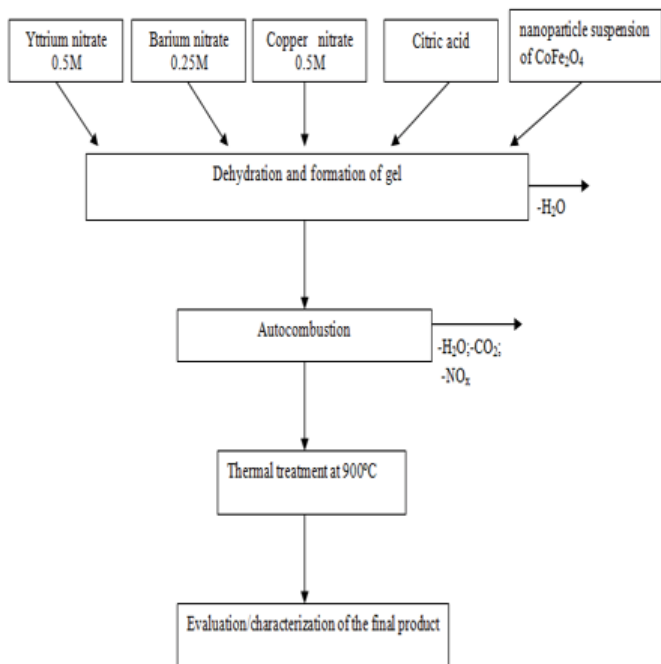


Fig. 1. Flow chart of the process for obtaining the composite material YBCO/ cobalt ferrite nanoparticles

detector (SAED). The microscope was operated in transmission mode at 300 kV; TEM point resolution was 2Å and line resolution was 1Å.

The room temperature magnetic susceptibility was measured on Lake Shore's fully integrated Vibrating Sample Magnetometer, VSM system 7404. SRM 2853/NIST and Ni sphere SRM 772a/NIST were used for VSM calibration. Also, $\text{CoHg}(\text{SCN})_4$ was used for intercalibration, between VSM and Faraday Balance.

Results and discussions

The X-ray diffraction analysis performed on the co-precipitation product shows that it is poorly crystallized, as can be seen from the diffractogram shown in figure 2.

Figure 3 shows HRTEM images for cobalt ferrite nanoparticles. As shown in the images are identified areas oriented on the surface of the sample. The ordering process, as expected, begins on the surface and the boundary of nanoparticles.

Elemental analysis performed on cobalt ferrite obtained by co-precipitation indicates the presence of Fe and Co, the sample not being contaminated with other elements during the synthesis process (fig. 4).

The XRD analysis performed on the citrate-nitrate autocombustion composite with the addition of cobalt ferrite nanoparticles reveals the presence of three phases YBCO 123 ($\text{YBa}_2\text{Cu}_3\text{O}_7$), BaCuO_2 and CoFe_2O_4 . The semi-quantitative analysis showed that the proportions are: YBCO 123-65%, BaCuO_2 -25% and CoFe_2O_4 -10%. The size of the nanoparticles calculated from the Scherer equation (assuming that all crystals are spherical and the shape factor associated with the shape is 0.89) is 39 nm (fig. 5).

The characteristic SEM images of the powder obtained after thermal treatment are presented in figure 6.

SEM images show a complex morphology with agglomerates of hundreds of nanometers, with layers deposited on agglomerates with granular morphology and with irregularly distributed intergranular spaces. The sample has non-uniform appearance identifying constitutive phases.

EDX analysis carried out on the YBCO / ferrite cobalt composite (fig. 7) obtained by citrate-nitrate autocombustion reveals the presence of the chemical elements Y, Ba, Cu, Co, Fe and the absence of organic residues, which is important for the applications of this material.

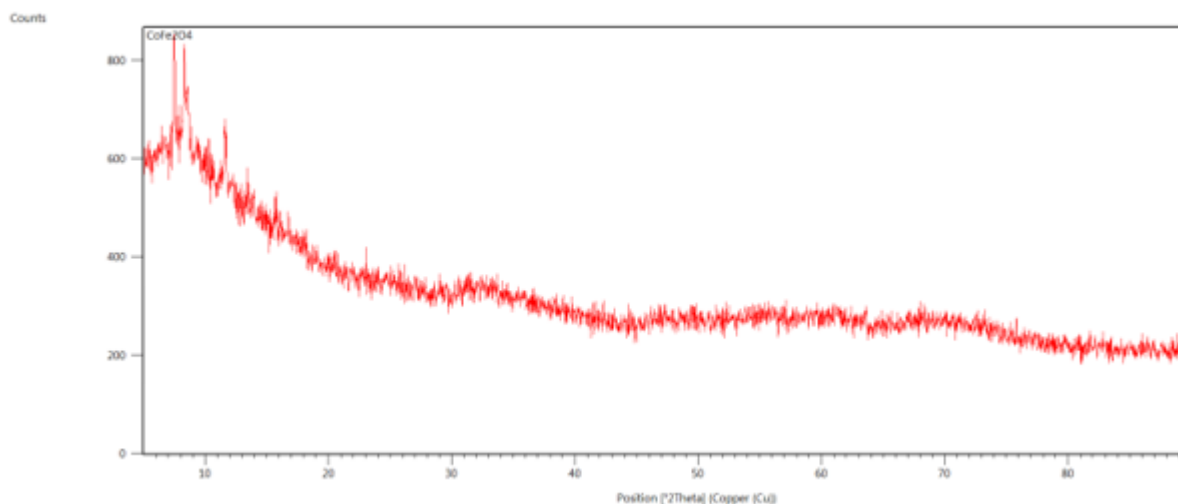


Fig. 2. XRD patterns of the cobalt ferrite nanoparticles

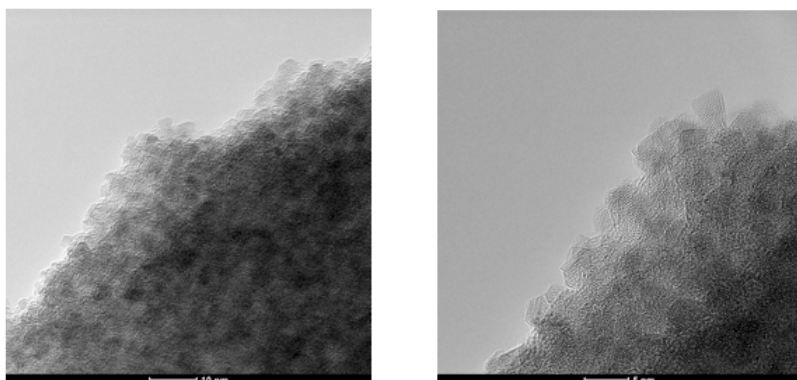


Fig. 3. Representative HRTEM images of cobalt ferrite nanoparticles

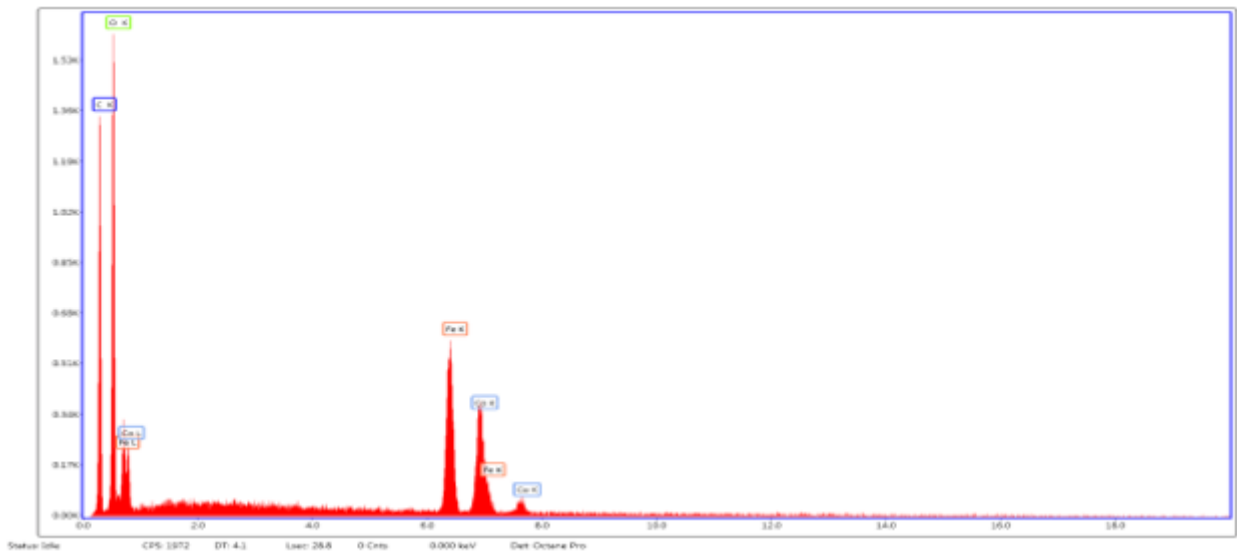


Fig. 4. EDX spectrum for CoFe_2O_4

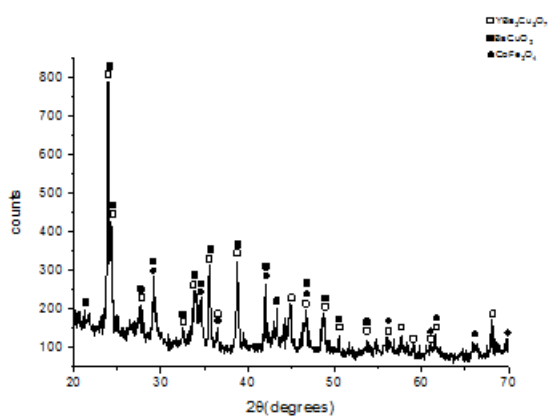


Fig. 5. XRD patterns of the composite $\text{YBCO}/\text{CoFe}_2\text{O}_4$

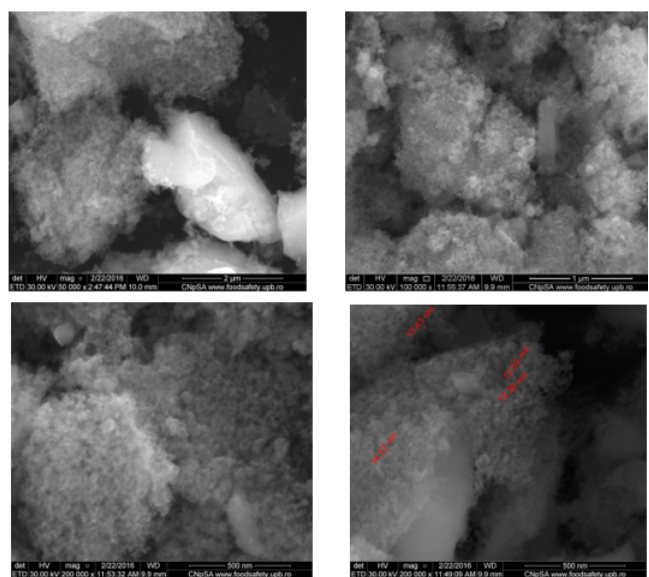


Fig. 6. Representative SEM images for composite $\text{YBCO}/\text{CoFe}_2\text{O}_4$

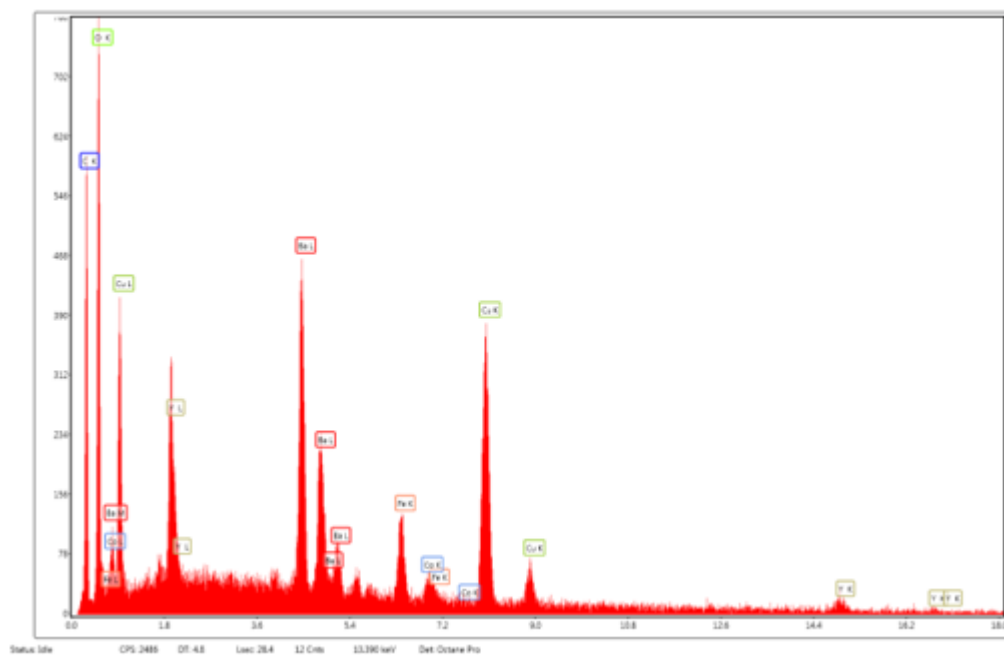


Fig. 7. EDX spectrum for composite $\text{YBCO}/\text{CoFe}_2\text{O}_4$

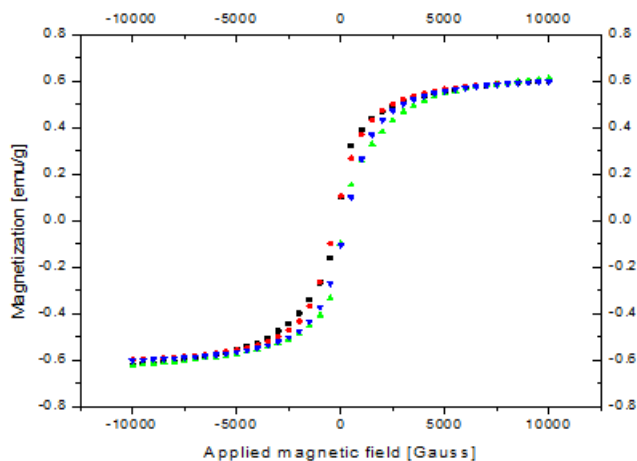


Fig. 8. The magnetization curve for the composite YBCO/CoFe₂O₄

The magnetization curve shown in figure 8 was obtained in a magnetic field of 1.5 T.

The sample was measured at 300 K and the maximum field applied was 1.5 T. Saturation magnetization obtained at room temperature was 0.64 emu/g. The sample shows superparamagnetic signal and nonlinear regression with Langevin function:

$$M_T(H) = M_S \left[\coth\left(\frac{H \bar{\mu}}{T k_B}\right) - \left(\frac{H \bar{\mu}}{T k_B}\right)^{-1} \right]$$

Conclusions

The core-shell composite material YBCO / CoFe₂O₄ was obtained using the citrate-nitrate autocombustion reaction with the addition of cobalt ferrite nanoparticles as a synthesis route. Cobalt ferrite was obtained by coprecipitation. The final obtained material was heated at 900 °C and then characterized. The material has polyhedral morphology with interconnected polyhedra and superparamagnetic signal at 300K.

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References

1. FIETZ, W. H., HELLER, R., SCHLACHTER, S.I., GOLDACKER, W., Fusion Engineering and Design, **86**, 2011, p 1365
2. YANG, W. M., CHAO, X.X., GUO, F. X., LI, J.W., CHEN, S.L., Physica C: Superconductivity, **493**, 2013, p 71
3. IWASA, Y., BASCUAN, J., SEUNGYONG, H., TOMITA, M., WEIJUN, Y., IEEE Transactions on Applied Superconductivity, **20**, 2010, p718.
4. CIOBANU, C.S., ANDRONESCU, E., PALL, L., ICONARU, S.L., GYORGY, E., PREDOI, D., Rev. Chim.(Bucharest), **61**, no. 12, 2010, p. 1207.
5. REN, H.T., TAYLOR, K.N.R., CHEN, Y.J., XIA, J.A., QING, H., Physica C, **216**, 1993, p 447.
6. SCHWARTZ, J., NAKAMAE, S., RABAN, G.W., HEUER, J.K., WU,S., WAGNER, J.L., HINKS, D.G., Physical Review B, **48**, 1993, p 9932.
7. SCHWARTZ, J. WU, S., Journal of Applied Physics, **73**, 1993, p 1343.
8. GUILMEAU, E., ANDRZEJEWSKI, B., NOUDEM, J.G., Physica C: Superconductivity, **387**, 2003, p 382.
9. JIA, Z.Y., TANG, H., YANG, Z.Q., XING, Y.T., WANG, Y.Z., QIAO, G.W., Physica C, **337**, 2000, p 130.
10. GUO, Y.C., TANAKA, Y., KURODA T., DOU, S.X., YANG, Z.Q., Physica C, **311**, 1999, p 65.
11. MA, R.C., SONG, W.H., ZHU, X.B., ZHANG,L., LIU, S.M., FANG, J., DU, J.J., SUN, Y.P., LI, C.S., YU, Z.M., FENG, Y., ZHANG, P.X., Physica C: Superconductivity, **405**, 2004, p 34.
12. GHATTAS, A., ANNABLM, ZOUAOU, M., AZZOUZ, FBEN, SALEM, M.BEN, Physica C: Superconductivity and its Applications, **468**, 2008, p 31.
13. SUNDARESAN A., RAO, C.N.R., Nano Today, **4**, 2009, p 96.
14. GHOSH CHAUDHURI, R., PARIA, S., Chem Rev, **112**, 2012, p 2373.
15. FICAI, D., FICAI, A., ALEXIE, M., MAGANU, M., GURAN, C., ANDRONESCU, E., REV. CHIM. (Bucharest) **62**, no. 6, 2011, p.622.
16. DE, M., GHOSH, P. S., ROTELLO, V.M., Advanced Materials, **20**, 2008, p 4225.
17. DANESHVAR, H., NELMS, J., MUHAMMAD, O., JACKSON, H., TKACH, J., DAVROS, W., PETERSON, T., VOGELBAUM, M. A., BRUCHEZ, M. P., TOMS, S. A., Nanomedicine, **3**, 2008, p 21.
18. PARK, J.I., CHEON, J., J. Am. Chem. Soc., **123**, 2001, p 5743 .
19. PARK, J.I., KIM, M. G., JUN, Y.W., LEE, J. S., LEE, W. R., CHEON, J., J. Am. Chem. Soc., **126**, 2004, p 9072.
20. REN, T.Z., YUAN, Z. Y., HU, W., ZOU, X., Microporous and Mesoporous Materials, **112**, 2008, p 467.

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