Multiferroic properties of $BiFeO_3/CoFe_2O_4$ multilayers structure at room temperature

Propiedades multiferroicas de la estructura multicapas $BiFeO_3/CoFe_2O_4$ a temperatura ambiente

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ABSTRACT

$BiFeO_3/CoFe_2O_4$ multilayer films were deposited by spin coating on Pt (Pt/TiO2/SiO2/Si) substrates and annealed at 700, 725 and 750 °C. The precursor of $BiFeO_3/CoFe_2O_4$ for multilayers structure was synthesized by chemical solution method. Patterns x-ray diffraction of the multilayers system revealed the composite-like structure. The leakage current was found less than 10^{-6} Amp at electric field below 100 kV/cm, which it shows the ohmic behavior of $BiFeO_3/CoFe_2O_4$. Dielectric constant decreases with increasing in the frequency range 103-106 Hz. $BiFeO_3/CoFe_2O_4$ system shows the co-existence of ferroelectric polarization (Pr) = 65 and 51 μC/cm2 and magnetization (Mr) =102 and 47 emu/cm3 at room temperature. Observed ferromagnetic and ferroelectric responses in multilayers system may be useful for bi-functional devices.

Key words: Multiferroic properties, multilayers structure, ferromagnetic and ferroelectric responses

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RESUMEN

Las películas multicapa $BiFeO_3/CoFe_2O_4$ se depositaron mediante recubrimiento por rotación sobre sustratos de Pt (Pt / TiO2 / SiO2 / Si) y se recocieron a 700, 725 y 750 ° C. El precursor de $BiFeO_3/CoFe_2O_4$ para la estructura de multicapas se sintetizó por el método de solución química. Los patrones de difracción de rayos X del sistema de multicapas revelaron la estructura de tipo compuesto. La corriente de fuga se encontró a menos de 10^{-6} Amp en el campo eléctrico por debajo de 100 kV / cm, que muestra el comportamiento óhmico de $BiFeO_3/CoFe_2O_4$. La constante dieléctrica disminuye al aumentar en el rango de frecuencia 103-106 Hz. El sistema $BiFeO_3/CoFe_2O_4$ muestra la coexistencia de polarización ferroeléctrica (Pr) = 65 y 51 μC / cm2 y magnetización (Mr) = 102 y 47 emu / cm3 a temperatura ambiente. Las respuestas ferromagnéticas y ferroeléctricas observadas en el sistema de multicapas pueden ser útiles para dispositivos bifuncionales.

Palabras clave: Propiedades multiferroicas, estructura de multicapas, respuestas ferromagnéticas y ferroeléctricas

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DOI: dx.doi.org/10.18050/RevUcv-Scientia.v9n2a4

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INTRODUCTION

Magnetism and ferroelectricity coexist in materials called multiferroics. The search for these materials is driven by the prospect of controlling charges by applied magnetic fields and spins by applied voltages, and using this to construct new forms of multifunctional devices[1] . The coupling between the corresponding order parameters was theoretically predicted long ago and is currently a topic of intense interest. However, single phase materials which simultaneously show high magnetization and polarization at ambient conditions remain elusive[2]. Thin film growth techniques that allow for the production of non-equilibrium phases of materials and strain engineering of existing materials for multiferroics. Thin films offer a pathway to the discovery and stabilization of a number of new multiferroics in conjunction with the availability of high quality materials that can be produced in larger lateral sizes than single crystal samples. Multiferroic thin films and nanostructures have been produced using a wide variety of growth techniques including sputtering, spin coating, pulsed laser deposition, sol–gel processes, metal–organic chemical vapor deposition, molecular beam epitaxy, and more[3]. (BFO) is a ferroelectromagnetic compound with uniquely high temperature of magnetic and electric ordering. That makes it a very prospective material for the applications in nonvolatile ferroelectric random access memory (NVFRAM), dynamic random access memory and sensors[4]. The room-temperature phase of BFO is classed as rhombohedral (point group R3c). The perovskite-type unit cell has a lattice parameter, a_{rh}, of 3.965Å and a rhombohedral angle, arh, of ca. 89.3–89.48° at room temperature, with ferroelectric polarization along $[111]_{pseudocubic}$[5]. The ferroelectric and antiferromagnetic ordering of $BiFeO_3$ are stable with Curie and Neél temperatures of 1098 and 643 K[6]. To improve its magnetic properties, attempts have been made to develop composite nanostructures with spinel ferrites (AB_2O_4). $CoFe_2O_4$ is an inverse spinel structure[7] have the general formula of AFe_2O_4 (where A2+: Co, Ni, Zn, etc.) and unit cell contains 32 oxygen atoms in cubic close packing with 8 tetrahedral (Td) and 16 octahedral (Oh) occupied sites. AFe_2O_4 has high coercivity and moderate magnetization, [8]and the space group Fd3-m composed of large unit cells[9].

In the present work, we have demonstrated that the ferroelectric and ferromagnetic exists in $BiFeO_3$-$CoFe_2O_4$(BFO-CFO), in an A/B/…A/B system multilayer thin film at room temperature on Pt (Pt/TiO2/SiO2/Si) substrate. It is revealed that the enhancements in ferromagnetic properties of BFO/CFO heterostructure are due to the presence of two separate phases of BFO and CFO. X-ray analysis indicate the presence of two separate phases of BFO and CFO.

MATERIALS AND METHODS

Bismuth nitrate pentahydrate $Bi(NO_3)_3.5H_2O$, iron (III) nitrate nanohydrate $Fe(NO_3)_3.9H_20$ were used as precursors for Bi and Fe, respectively, for the formation of 0.03 molar solution of $BiFeO_3$. Cobalt (II) nitrate hexahydrate $Co(NO_3)_2.6H_2O$ and iron (III) nitrate nanohydrate $Fe(NO_3)_3.9H_20$ were used as precursors for Co and Fe, respectively, to achieve 0.08 molar solution of $CoFe_2O_4$. Due to the volatilization of Bi element during annealing, we weighed $Bi(NO_3)_3.5H_2O$ with 10% mol excess to compensate for the Bi loss. BFO and CFO were dissolved in the 2-methoxyethanol and stirred at 60°C for 2h each separately. The solution containing $BiFeO_3$ and $CoFeO_2$ was spin coated at 5000 rpm for 30sec. on Pt (Pt/TiO2/SiO2/Si) substrate. Each coated layer was dried on a hot-plate at 300 °C for 10 min. Then, coated film was rapidly thermally annealed at three different temperatures (700, 725 and 750 °C) for 10 min in air environment. Finally, the solution containing $CoFe_2O_4$ was similarly coated, dried, and annealed at three different temperatures on $BiFeO_3$ covered surface. The structure was given a final rapid thermal anneal at 700, 725 and 750°C for 10 min; and the last layer of 30 min.

RESULTS AND DISCUSSION

X- ray diffraction patterns of the BFO/CFO and CFO-BFO films deposited on Pt substrate (Pt/Ti/SiO2/Si). Fig.1(a) mixed is shown in Fig.1(a) at different temperatures (700, 725 and 750°C). Fig. 1 (b) show diffraction peaks for BFO and CFO suggests the formation of rhombohedral perovskite and spinel.

In Fig.1(a) show the dominant x-ray diffraction peaks (101), (102), (110), (202), (113), (211) and (122) of $BiFeO_3$, (220), (102), (222), (400) and (311) peaks of $CoFe_2O_4$ co-exist in the multilayer structure. We have estimated the crystallite size D of the samples from peak with miller indices by (311) of CFO and (110) of BFO respectively, using Scherrer equation[10]:

$$D=(0.9)\lambda/\beta\cos\theta \qquad (1)$$

Where, D is the grain diameter, β is half intensity width of the relevant diffraction, λ is X-ray wavelength and θ the diffraction angle. The lattice parameter was calculated according to the Eq. (2) and (3) for CFO and BFO (α =89.3°), respectively:

parameter was calculated according to the Eq. (2) and (3) for CFO and BFO (α =89.3°), respectively:

$$a = d_{hkl}(h^2 + k^2 + l^2) \qquad (2)$$

$$a^2 = \frac{d_{hkl}{}^2[(h^2+k^2+l^2)\sin^2\alpha+2(hk+kl+hl)(\cos^2\alpha+\cos\alpha)]}{\alpha^2(1-3\cos^2\alpha+2\cos^3\alpha)} \qquad (3)$$

As shown the lattice parameter estimated from the strongest diffraction peak of (311) and (110) is 8.374, 8.383 and 0.8391 Å for the CFO and 3.963, 3.964 and 3.969 Å for BFO respectively. These values are close to the known bulk of $CoFe_2O_4$ (8.39570 Å)[11] and of $BiFeO_3$ (3.965 Å)[5].

Tabla 1. The crystallite size and lattice constant of BFO and CFO at different temperature.

Temperature(°C)	Lattice Parameter (nm)		Cristallite size (nm)	
	BFO	CFO	BFO	CFO
700	0.3963	0.8374	49.146	27.07
725	0.3964	0.8383	45.641	27.13
750	0.3969	0.8391	36.528	29.3

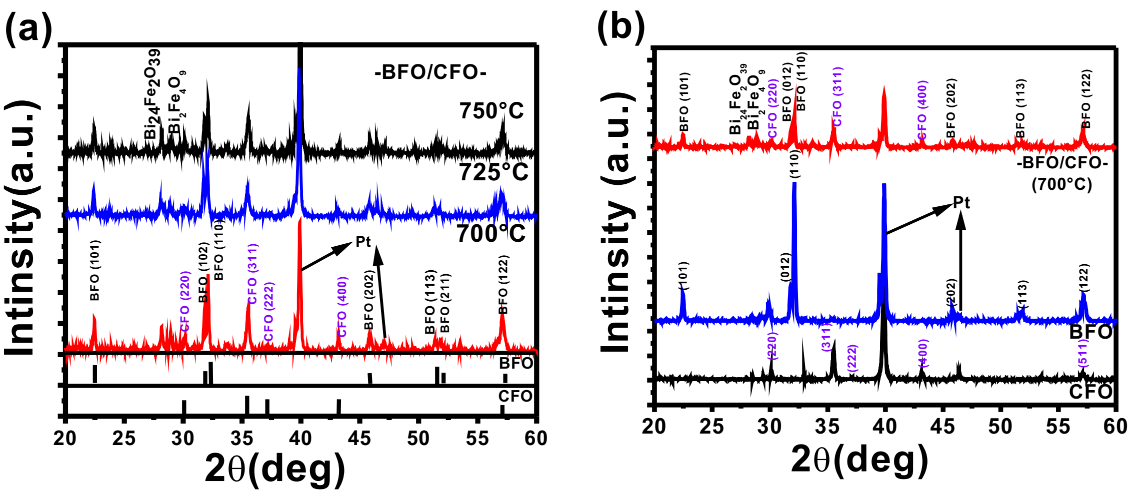

Figura 1. X-ray diffraction patterns: (a) $BiFeO_3$-$CoFe_2O_4$ thin films at different temperatures and (b) $CoFe_2O_4$, $BiFeO_3$ films and $BiFeO_3$-$CoFe_2O_4$ multilayers structures at 700°C on Pt substrate (Pt/TiO2/SiO2/Si).

SEM

Fig. 2 shows the scanning electron microscopy (SEM) images of BFO/CFO layers, which shows a polycrystalline nature of film.

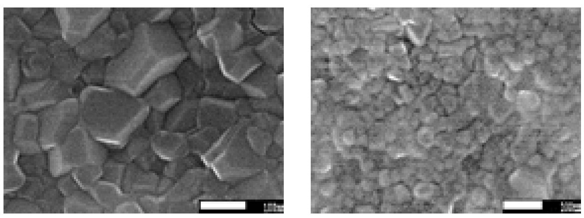

Figura 2. Micrograph showing surface morphology of the $BiFeO_3/CoFe_2O_4$ structure at different temperature: (a) 700 and (b) 750°C

Ferroelectric and Ferromagnetic measurements:

The top electrode of Pt (3 x10^4 cm^2), with the structures of Pt/BFO-CFO/Pt/Ti/SiO2 /Si was fabricated, it was deposited by dc sputtering using mechanical mask for the measurements of leakage current, dielectric, and ferroelectric responses. Fig.3 showed the leakage current (J) as a function of applied dc electric field on the capacitor structure.

The leakage current response was measured using digital electrometer (Keithley 6514). In electroceramics such as BiFeO3 leakage current was controlled by the bulk state, i.e., ohmic behavior in low fields, and in the intermediate field grain boundaries regions may be effective, but in very large fields, space charge limited current (SCLC) and electrode-film interface resistance may dominate[12-14]. It can be seen that the leakage current densities of the BFO thin films are much lower than those of the pure BFO thin films. The measured leakage current densities of the pure BFO/CFO thin films are 10^{-4} A/cm^2 for the film with annealing at 700 and 750°C at an applied electric field of 140 kV/cm, respectively. The result is similar to that of the other reports[13]. The BFO thin film exhibits the low resistance because of the oxygen vacancies and iron valence (Fe^{2+}, Fe^{3+}), as well as from various defects such as stoichiometry, grain boundaries and pores present in the films.

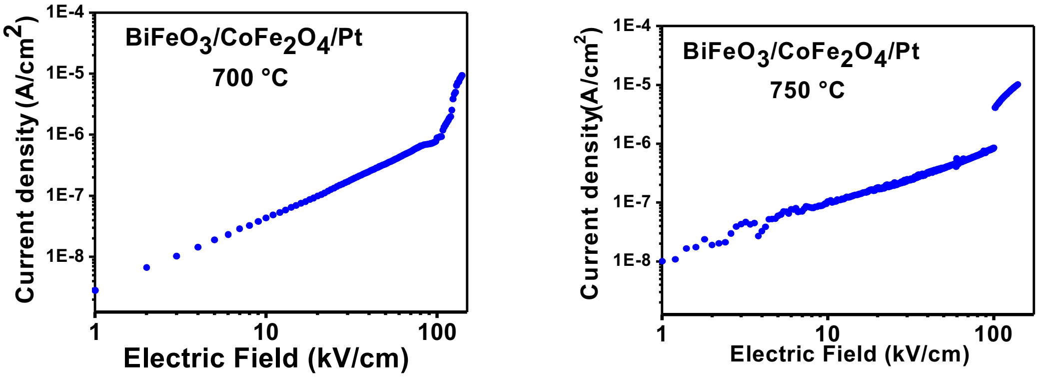

Figura 3. Leakage current versus electric field of the $BiFeO_3/CoFe_2O_4$ structure at different temperature.

Fig. 4 shows the dielectric constant and dielectric loss (tanδ) of BFO/CFO multilayer films with variation of ambient temperature in the frequency range (10^3 –10^6Hz). The dielectric constant decreases with increasing frequency as expected. However, the dielectric loss (tan δ) maximizes at 10^5Hz and minimizes to less at 10^6Hz. Observed relaxation may be due to different resistivity and permittivity of the layers involved. Fig. 5, show the magnetic hysteresis (M-H) of $BiFeO_3$-$CoFe_2O_4$ thin films, measured by VSM at room temperature. It is demonstrated that the magnetic properties of samples which were deposited by spin coating with annealing at different temperatures (700 and 750°C).

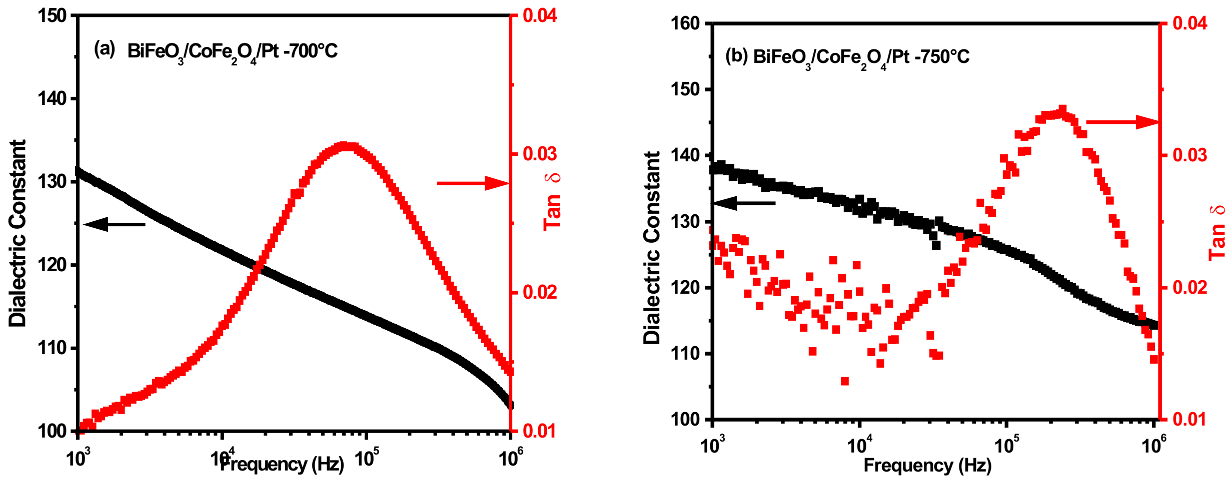

Figura 4. Dielectric constant versus frequency response of the $BiFeO_3/CoFe_2O_4$ structure at different temperatures (a) 700 and (b) 750 °C.

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The sample, which was annealed at 700°C having saturation magnetization, Ms, 260 emu/gr and remnant magnetization, Mr,102 emu/gr, respectively, as show in the Table2.

Tabla 2. Magnetic properties of samples annealing at different temperatures.

Temperature (°C)	Ms (emu/gr)	Mr (emu/gr)	Hc (Oe)	R
700	260	102	1230	0.39
750	136	47	2110	0.32

The remnant ratio R=Mr/Ms is an indication of the ease with which the direction of magnetization reorients to the nearest easy axis magnetization direction after the magnetic field is removed. The values of the remnant ratio of the prepared samples are in the range 0.32–0.39. The low value of R is an indication of the isotropic nature of the material[15].

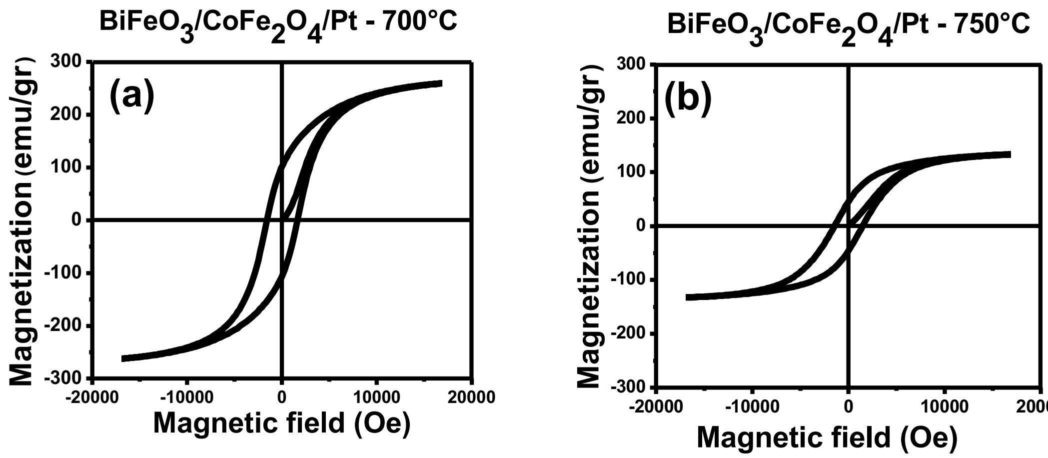

Figura 5. M-H curve of the $BiFeO_3$-$CoFe_2O_4$ films at different temperatures (a) 700 and (b) 750°C

With top and bottom Pt contacts, the ferroelectric response was measured by RT 6514 HVS tester and is shown in Fig. 6. Well saturated ferroelectric response and remnant polarization (Pr) = 65 and 49 μC/cm^2 at different temperatures respectively was observed at room temperature.

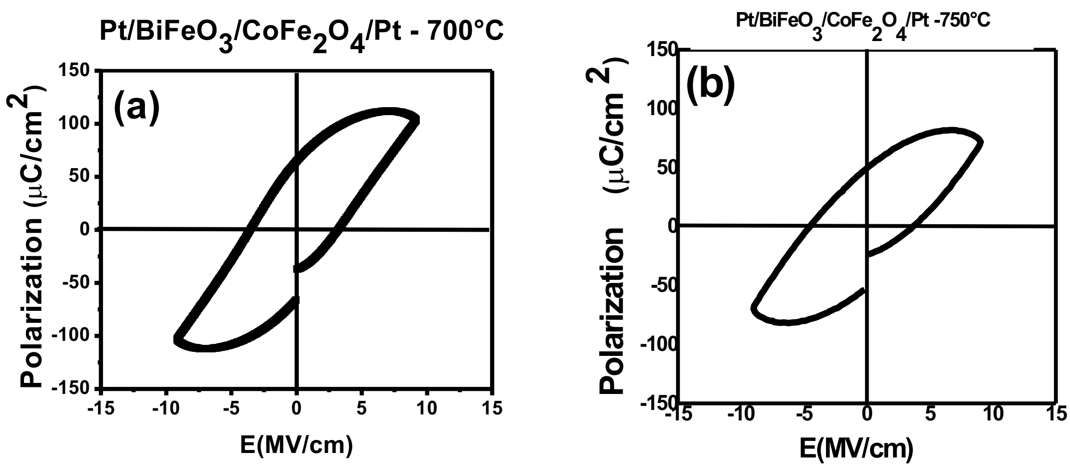

Figura 6. Ferroelectric hysteresis loop of Pt/ $BiFeO_3$/$CoFe_2O_4$/Pt bilayer structure at different temperatures (a) 700 and (b) 750°C.

REFERENCES

1. S.W. Cheong and M. Mostovoy, Multiferroics: a magnetic twist for ferroelectricity, Nature Materials, 2007 6 13-20.
2. F. Zavaliche, H. Zheng, L. Mohaddes-Ardabili, S.Y. Yang, Q. Zhan, P. Shafer, E. Reilly, R. Chopdekar, Y. Jia, P. Wright, D.G. Schlom, Y. Suzuki, and R. Ramesh, Electric Field-Induced Magnetization Switching in Epitaxial Columnar Nanostructures, Nano Lett., 2005 5 1794-1796.
3. L.W. Martin, S.P. Crane, Y-H Chu, M.B. Holcomb, M. Gajek, M. Huijben, C-H Yang, N. Balke and R. Ramesh, Multiferroics and magnetoelectrics:thin films and nanostructures, J. Phys.: Condens. Matter 2008 20 434220.
4. A.Z. SimÖes, C.S. Riccardi, M.L. Dos Santos, F.G. Garcia, E. Longo and J.A. Varela, Effect of annealing atmosphere on phase formation and electrical characteristics of bismuth ferrite thin films, Materials Research Bulletin 2009 44 1747–1752.
5. Gustau Catalan and James F. Scott, Physics and Applications of Bismuth Ferrite, Adv. Mater. 2009 21 2463–2485.
6. Oliver Clemens, Robert Kruk, Eric A. Patterson, Christoph Loho, Christian Reitz, Introducing a Large Polar Tetragonal Distortion into Ba-Doped BiFeO3 by Low-Temperature Fluorination, Inorg. Chem. 2014 53 12572–12583.
7. A.K. Axelsson, F. Aguesse, V. Tileli, M. Valant, Neil McN. Alford, Growth mechanism and magnetism of CoFe2O4 thin films; Role of the substrate, Journal of Alloys and Compounds, 2013 578 286–291.
8. S.A. Khorrami1, Q.S. Manuchehri, Magnetic properties of Cobalt Ferrite synthesized by Hydrothermal and Co-precipitation Methods: A Comparative Study, Journal of Applied Chemical Research, 2013 7 15-23.
9. L. Kumar, P. Kumar, A. Narayan and M. Kar, Rietveld analysis of XRD patterns of different sizes of nanocrystalline cobalt ferrite, International Nano Letters 2013 3 8.
10. S. Prasad, A. Vijayalaksshimi, N.S. Gajbhiye, thermal hydrolysis as a new method of synthesis of the CoFe2O4 spinel ferrite, J. Therm. Anal., 1998 52 595.
11. G. Bate,Ferromagnetic Materials, E.P. Wohlfarth (Ed.), 1980 2 431.
12. A.Z. Simoes, C.S. Riccardi, M.L. Dos Santos, F. Gonzalez Garcia, E. Longo, J.A. Varela, Effect of annealing atmosphere on phase formation and electrical characteristics of bismuth ferrite thin films, Materials Research Bulletin 2009 44 1747–1752.
13. G. Dong, G. Tan, Y. Luo, W. Liu, Ao Xia, H. Ren, A comparative investigation on structure and multiferroic properties of bismuth ferrite thin films by multielement co-doping, Materials Research Bulletin 2014 60 596–603
14. Y. Fuxue, Z. Gaoyang, S. Na, Sol-gel preparation of La-doped bismuth ferrite thin film and its low-temperature ferromagnetic and ferroelectric properties, Journal of Rare Earths 2013 31 1.
15. B.G Toksha, S.E. Shirsath, S.M. Patange, K.M. Jadhav, Structural investigations and magnetic properties of cobalt ferrite nanoparticles prepared by sol-gel auto combustion method, Solid State Commun. 2008 147 479–483.

Recibido: 15 de agosto 2017 **|** **Aceptado:** 19 de septiembre2017