

MICROWAVE STUDIES OF FERRITE-FERROELECTRIC COMPOSITES PREPARED THROUGH SELF PROPAGATING AUTO COMBUSTION ROUTE

M. B. Shelar, R. N. Jadhav, and V. Puri

Thick and Thin Film Device Lab, Department of Physics
Shivaji University, Kolhapur 416004, India

Abstract—The structural and microwave properties of (y) $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ and $(1 - y)$ $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4, 0.6$ and $y = 0.15, 0.30$ and 0.45) composites synthesized by self propagating auto combustion route was studied. X-ray diffraction patterns reveal this method can produce two phases simultaneously. The porosity increases with increase in ferrite content in the composite. The SEM morphologies show the growth of cadmium substituted nickel ferrite grains which are well dispersed in barium strontium titanate (BST) matrix. The composite material shows microwave absorption of about 0.575 in a broad band from 8–12 GHz. The permittivity varied from 7 to around 43 with increase in ferrite content. The microwave conductivity measurements reveal the loss of polaron conduction which supports the dielectric loss in the microwave region.

1. INTRODUCTION

Materials which can absorb microwaves can eliminate electromagnetic wave pollution. Wide spread applications of electromagnetic absorbers, have inspired engineers to explore about optimal design with available algorithms. Ideally a thin, light weight and wideband absorber is an optimum one [1]. Many types of the magnetic microwave devices have been devised with dielectric and magnetic substrates [2]. The presences of magnetic material in the propagating structure results in energy losses due to eddy currents which significantly dampen the electromagnetic waves, thus, the composite with high value of saturation magnetization of ferromagnetic material with extremely low electrical conductivity are used to for microwave tunable devices. One

can fabricate the phase shifter with frequency agile materials whose electromagnetic parameters can be changed by applying magnetic field composite [3].

The efforts so far on such composites have primarily focused on low frequency (10 Hz–1 kHz) phenomena [4–6]. An adaptive controlled system which can enhance the performances of a wireless system also requires the tunable devices and circuits such as tunable phase shifters and tunable filters [7, 8]. The magnetic tuning could be achieved over a very wide frequency range, but is relatively slow, noisy, and requires high power for operation. Therefore the devices but with some unique advantages could be realized by replacing the ferrite with a ferrite-ferroelectric composite [9] for the enhanced output in microwave tunable filters. Many techniques have been developed to measure the permittivity [10–12]. The complex permittivity is an important factor which can be altered to achieve maximum absorption of the electromagnetic waves.

Most of the known single phase bulk magnetoelectric (ME) materials do not exhibit strong ME coupling, have Néel or Curie temperatures far below room temperature, and also difficult to grow in thin film form [13]. The extrinsic ME response in the composites is due to the composite effect of the two phases, implying that a property like magnetoelectric effect can be induced in two different phases. Zheng et al. [14] have successfully demonstrated growth of self-assembled nanopillars of magnetostrictive material (CoFe_2O_4) in a piezoelectric BaTiO_3 matrix by Pulsed Laser Deposition (PLD). Hence, looking into the inexpensive methods of preparation the composite using self propagating auto combustion route was synthesized. The auto combustion process is different from pyrolysis techniques since once ignited it does not require external heating.

In the present paper, the studies on morphological and microwave properties of (y) $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 + (1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4, 0.6$ and $y = 0.15, 0.30$ and 0.45) composites prepared through the self propagating auto combustion route is reported. To the authors knowledge there are no reports on the composites of ferrite-ferroelectric containing cadmium as a non-magnetic material using this method. The cadmium has high value of dielectric constant, low eddy current losses, high electrical resistivity and high value of saturation magnetization which may useful for microwave tunable devices.

2. EXPERIMENTAL PROCEDURE

The high purity AR grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used to prepare $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6$).

The raw material is heated to evolve NO_2 , CO_2 and H_2O at 80°C . The 10% PVA (polyvinyl alcohol) and sucrose were added to the nitrates solution. The sucrose acts as a fuel for the combustion purpose and that of PVA is to form polymer regions with the metal ions trapped in it. The dried and fluffy gel gets burnt in self-propagating combustion manner at about 200°C . The prepared ash was calcined at 600°C for 6 hours. The same procedure was followed to make $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ by using $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Ti}(\text{NO}_3)_2$ as a precursor. The prepared ash was calcined at 900°C for 10 hours. The mixture of (y) $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 + (1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4, 0.6, y = 15\%$ (0.15), 30% (0.30) and 45% (0.45)) were uniaxially pressed into pellets and annealed at 950°C for 9 hours.

The crystalline phase of the samples was determined by XRD (Model-PW-3710) with $\text{Cu-k}\alpha$ radiation. The microstructures were characterized by SEM (Model-JEOL JSM 6360). Microwave absorption was studied in the X-band (8–12 GHz) using the waveguide reflectometer set-up [15]. The permittivity at microwave frequency was measured by using Voltage Standing Wave Ratio (VSWR) slotted section method. By measuring the displacements of maxima and minima, the permittivity of the composite has been determined. The real and imaginary parts of the permittivity were calculated by using Smith chart [16].

3. RESULTS AND DISCUSSIONS

Figure 1 shows the coexistence with good compatibility with each other of (y) $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ and $(1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ sample confirmed by X-ray Diffraction pattern. The intensity of ferrite peaks increases with its percentage in constituent composite phase.

The change in structure was not observed for individual phase in the composite. The XRD pattern for other composition of ferrite in the composite has already been reported in our previous paper [17]. The (110) and (311) peak shows presence of both perovskite and cubic phase. The x-ray diffraction pattern reveals that the intensity as well as number of the ferrite peaks decreases on increasing the ferrite content [18].

Knowing the values for x-ray density and actual density, the percent porosity of the composites can be calculated

$$\text{Porosity}(\%) = \frac{d_X - d_a}{d_X} \times 100$$

where, d_X = X-ray density and d_a = Actual density of composite.

The x-ray density and the percent porosity variation as a function of Cd content for all the series are shown in Figs. 2(a) and (b)

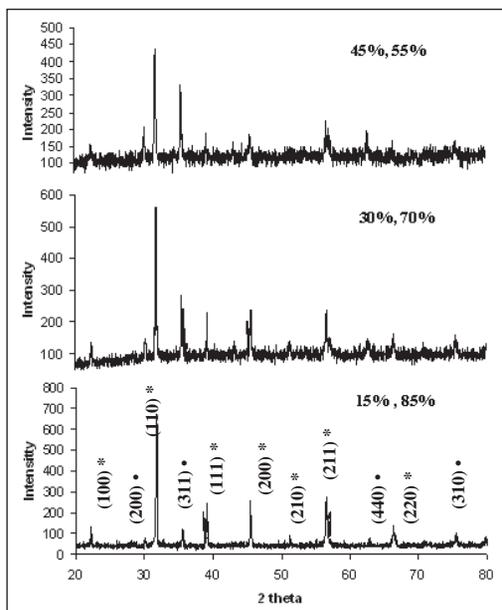


Figure 1. XRD pattern for (y) $\text{Ni}_{0.8}\text{Cd}_{0.2}\text{Fe}_2\text{O}_4 + (1 - y)$ $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ composite, * $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ phase, • $\text{Ni}_{0.8}\text{Cd}_{0.2}\text{Fe}_2\text{O}_4$ phase.

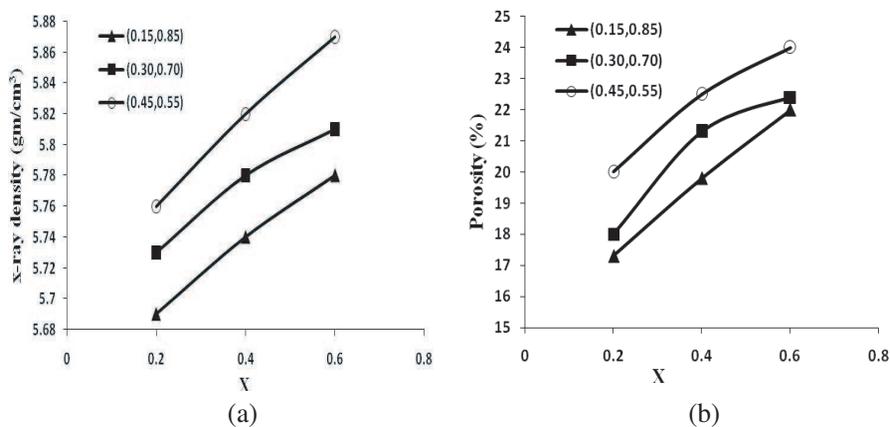


Figure 2. Variation of (a) x-ray density and (b) porosity with Cd content.

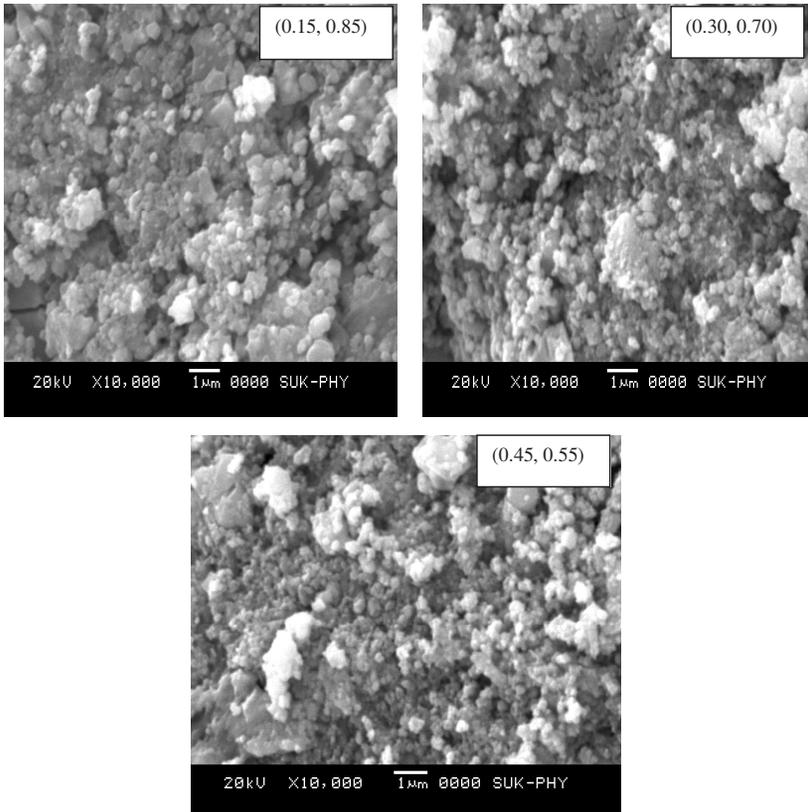


Figure 3. SEM micrographs pattern for $(y) \text{Ni}_{0.8}\text{Cd}_{0.2}\text{Fe}_2\text{O}_4 + (1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ composite.

respectively. As the Cd content increases the x-ray density and porosity increases. Also it is seen that as the density of ferrite phase increases in the composite the density and porosity increases. The porosity for the entire sample lies in the range of 17% to 25%. The maximum porosity for $(0.45) \text{Ni}_{0.4}\text{Cd}_{0.6}\text{Fe}_2\text{O}_4$ ferrite + $(0.55) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ composite of 24.16% was observed among all the studied samples. The increase in porosity may be responsible to lower the conductivity of the materials in the microwave region.

Figure 3 shows the SEM micrographs for $(y) \text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ and $(1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2$ and $y = 0.15, 0.30$ and 0.45) samples. It reveals the agglomeration of ferrite grains with ferroelectric grains with average size about 200 nm. This may be due to interaction of small sized ferroelectric grains with ferrite grain.

Table 1. Variation of grain size of the constituent phase and their composites.

Composition (y)	Average grain size (μm)
$(y) \text{Ni}_{0.8}\text{Cd}_{0.2}\text{Fe}_2\text{O}_4 + (1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$	
0.15	1.25
0.30	0.46
0.45	0.30
$(y) \text{Ni}_{0.6}\text{Cd}_{0.4}\text{Fe}_2\text{O}_4 + (1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$	
0.15	1.05
0.30	0.90
0.45	0.10
$(y) \text{Ni}_{0.4}\text{Cd}_{0.6}\text{Fe}_2\text{O}_4 + (1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$	
0.15	0.50
0.30	0.32
0.45	0.17

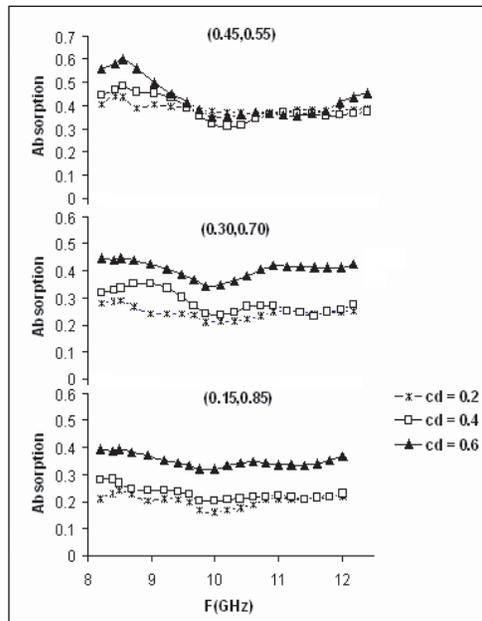


Figure 4. Microwave absorption of $(y) \text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ and $(1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4, 0.6$ and $y = 0.15, 0.30$ and 0.45).

The average grain size of composites goes on decreasing with increase in ferrite content. Larger grain size of ferroelectric phase as compared to ferrite phase can effectively reduce the leakage of electric charges induced by the chain formation of ferrite phase particles. Table 1 gives the dependence of grain size of the constituent phase and their composites.

Figure 4 shows the microwave absorption of (y) $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ and $(1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4$ and $0.6, y = 0.15, 0.30$ and 0.45). The increase in cadmium in ferrite phase increases the absorption of microwaves. At $x = 0.6$ the absorption increases up to 0.59 at frequency 8.5 GHz. The presence of cadmium in ferrite increases the grain boundaries which would be responsible for the increase in the absorption.

Figures 5(a) and 5(b) shows the graphs of real (ϵ') and imaginary (ϵ'') parts of the permittivity of (y) $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 + (1-y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4$ and $0.6, y = 0.15, 0.30$ and 0.45). The

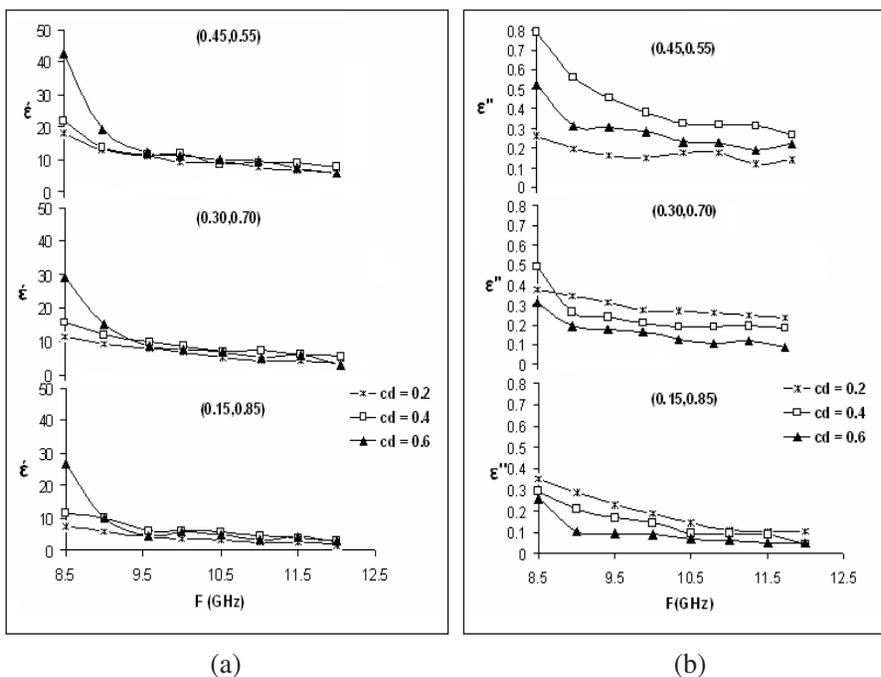


Figure 5. (a) Real part (ϵ') and (b) Imaginary part (ϵ'') of permittivity for (y) $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 + (1 - y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4, 0.6$ and $y = 0.15, 0.30$ and 0.45).

real and imaginary parts of dielectric constant were calculated using the Clapham equation [19].

$$\varepsilon' = \left(1 + \frac{\Delta\phi \times \lambda_0}{360 \times d}\right)^2 \quad \text{and} \quad \varepsilon'' = \left(\frac{\Delta A \lambda_0 \sqrt{\varepsilon'}}{8.686\pi d}\right)$$

where, $\Delta\phi$ = Phase angle in degree, λ_0 = Guided wavelength, d = Thickness of film

ΔA = Difference in attenuation in dB

A sharp decreases in dielectric constant is observed between 8.5 and 9.5 GHz, beyond which the decrease is very small. The value for ε' for $(y) \text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 + (1-y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4, 0.6$ and $y = 0.15, 0.30$ and 0.45) varies from 7 to 43. The maximum value of ε' observed for $(0.45) \text{Ni}_{0.4}\text{Cd}_{0.6}\text{Fe}_2\text{O}_4 + (0.55) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ was about 42.59. High value of permittivity at lower frequency is observed due to maximum accumulated charge carriers at the interface [20].

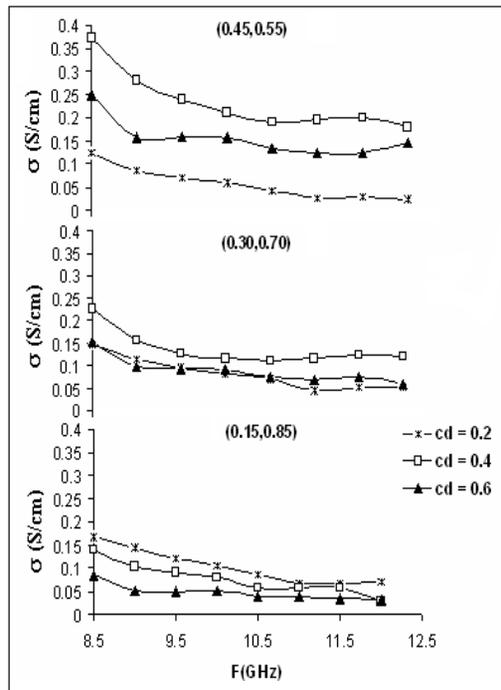


Figure 6. Microwave conductivity for $(y) \text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 + (1-y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$.

The imaginary part of permittivity which has a similar nature as that of real part with frequency and becomes almost constant beyond 11 GHz. The increased content of ferrite increases the dielectric relaxation at lower frequencies around 0.80.

Figure 6 shows the microwave conductivity for $(y) \text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 + (1-y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4, 0.6$ and $y = 0.15, 0.30$ and 0.45). The increase in content of ferrite in composite increases the interaction of electrons with lattice ions through long range forces. Lower value of conductivity of $\sim 0.25 \text{ S/cm}$ is observed for $(0.45) \text{Ni}_{0.4}\text{Cd}_{0.6}\text{Fe}_2\text{O}_4 + (0.55) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ composition.

The resulting interaction produces lattice polarization acts as a potential well. This hinders the movement of an electron and hence decreases the mobility of the material. This indicates the loss of polaron type of conduction which supports the dielectric loss in microwave region. This lower value of conductivity is suitable composition for the microwave tunable devices [21].

4. CONCLUSION

A series of $(y) \text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ and $(1-y) \text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.2, 0.4, 0.6$ and $y = 0.15, 0.30, 0.45$) composites were prepared by self propagating auto combustion route and characterized using X-ray diffraction and SEM technique. The increase in porosity of ferrite lowers the microwave conductivity of the composite. The increased content of cadmium in ferrite phase permits the higher absorption of microwaves. The higher dielectric constant observed in turn decreases with increase in ferrite content. Lowering the dielectric loss value supports the microwave tunable devices operation. The decrease in microwave conductivity from 0.37 to 0.24 S/cm shows the loss of polaron type of conduction in microwave region.

ACKNOWLEDGMENT

One of the authors Dr. Vijaya Puri is gratefully acknowledged to UGC for the award of research scientist 'C'.

REFERENCES

1. Chamaani, S., S. A. Mirtaheri, M. Teshnehlab, M. A. Shoorehdeli, and V. Seydi, "Modified multi-objective particle swarm optimization for electromagnetic absorber design," *Progress In Electromagnetics Research*, Vol. 79, 353–366, 2008.

2. Oates, D. E. and G. F. Dionne, "Tunable YBCO resonators on YIG substrates," *IEEE Transactions on Applied Superconductors*, Vol. 7, 2338–2342, 1997.
3. How, H., P. Shi, C. Vittoria, L. C. Kempel, and K. D. Trott, "Single-crystal YIG phase shifter using composite stripline structure at X band," *Journal of Applied Physics*, Vol. 87, 4966–4968, 2000.
4. Srinivasan, G., E. T. Rasmussen, J. Gallegos, R. Srinivasan, Yu. I. Bokhan, and V. M. Laletin, "Magnetolectric bilayer and multilayer structures of magnetostrictive and piezoelectric oxides," *Physics Review B*, Vol. 64, 214408, 2001.
5. Zhai, J., J. Li, D. Viehland, and M. I. Bichurin, "Large magneto electric susceptibility: The fundamental property of piezoelectric and magnetostrictive laminated composites," *Journal of Applied Physics*, Vol. 101, 014102, 2007.
6. Shi, Z., Y. Lin, and C.-W. Nan, "Magnetolectric resonance behavior of simple bilayered Pb (Zr, Ti(O₃– (Tb,Dy) Fe₂/epoxy composites," *Journal of Applied Physics*, Vol. 101, 043902, 2007.
7. Hong, J.-S. and Y.-H. Chun, "On the development of tunable microwave devices for frequency agile applications," *PIERS Online*, Vol. 4, No. 7, 726–730, 2008.
8. Chun, Y. H., J.-S. Hong, P. Bao, T. J. Jackson, and M. J. Lancaster, "BST-varactor tunable dual-mode filter using variable Z_C transmission line," *IEEE Microwave and Wireless Components Letters*, Vol. 18, 167–169, 2008.
9. Tatarenko, A. S., M. I. Bichurin, and G. Srinivasan, "Electrically tunable microwave filters based on ferromagnetic resonance in single crystal ferrite-ferroelectric bilayers," *Electronic Letters*, Vol. 41, 596–597, 2005.
10. Chou, Y.-H., M.-J. Jeng, Y.-H. Lee, and Y.-G. Jan, "Measurement of RF PCB dielectric properties and losses," *Progress In Electromagnetics Research Letters*, Vol. 4, 139–148, 2008.
11. He, X., Z.-X. Tang, B. Zhang, and Y. Wu, "A new deembedding method in permittivity measurement of ferroelectric thin film material," *Progress In Electromagnetics Research Letters*, Vol. 3, 1–8, 2008.
12. Jadhav, R. N. and V. Puri, "Microwave absorption, conductivity and complex permittivity of fritless Ni_(1-x)Cu_xMn₂O₄ ($0 \leq x \leq 1$) ceramic thick film: Effect of copper," *Progress In Electromagnetic Research C*, Vol. 8, 149–160, 2009.
13. Schmid, H., "On ferrotoroidics and elastotoroidic, magneto-

- toroidic and piezotoroidic effects,” *Ferroelectrics*, Vol. 252, 41–50, 2001.
14. Zheng, H., J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, and R. Ramesh, “Multiferroic BaTiO₃-CoFe₂O₄ Nanostructures,” *Science*, Vol. 303, 661–663, 2004.
 15. Vhankhande, B. B., S. V. Jadhav, D. C. Kulkarni, and V. Puri, “Investigations on the microwave properties of electropolymerised polyaniline thin film,” *Microwave Optical Technology Letters*, Vol. 50, 761–766, 2008.
 16. Adam, S. F., *Microwave Theory and Applications*, 392, Prentice Hall, New Jersey, 1969.
 17. Shelar, M. B., P. A. Jadhav, B. K. Chougule, and V. R. Puri, “Structural and dielectric behavior of (y) Ni_{1-x}Cd_xFe₂O₄ + (1 - y) Ba_{0.8}Sr_{0.2}TiO₃ magnetoelectric composites prepared through SHS route,” *International Journal of Self Propagating High Temperature Synthesis*, Vol. 19, 102–109, 2010.
 18. Patankar, K. K., V. L. Mathe, R. N. Patil, and B. K. Chougule, “Structural analysis, magnetic properties and magnetoelectric effect in piezomagnetic–piezoelectric composites,” *Materials Chemistry and Physics*, Vol. 96, 197–200, 2006.
 19. Kulkarni, D. C. and V. Puri, “Ku band microwave studies of fritless strontium hexaferrite thick films,” *Microelectronics International*, Vol. 27, 143–147, 2010.
 20. Devan, R. S., Y. D. Kolekar, and B. K. Chougule, “Effect of cobalt substitution on the properties of nickel–copper ferrite,” *Journal of Physics: Condensed Matter*, Vol. 18, 9809–9810, 2006.
 21. Chun, Y. H., J.-S. Hong, P. Bao, T. J. Jackson, and M. J. Lancaster, “BST varactor tuned band stop filter with slotted ground structure,” *2008 IEEE MTT-S*, 2008.