Microstructure Induced Tunable Magnetocapacitance Response of Barium Titanate-Ferrite Composite Systems

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Abstract

Magnetic and dielectric properties exhibited by magneto-dielectric composite systems can be tunable using electrical and magnetic fields due to mechanical coupling effect, which may led to potential application such as electrically readable magnetic memories, phase shifters, miniature antennas and magnetic sensors. The mechanical coupling effect strongly depends on morphology of the phases (magnetic and dielectric) present in the composites along with their orientation and interaction, which can be altered by using a novel auto-combustion derived ex-situ synthesis technique. The prime objective of this research work was to tailor the microstructure as well as tune the magnetocapacitance, an important property of the magneto-dielectric composite. In the above synthesis technique, the calcined powder (derived via auto-combustion) of one phase of composite was added in the solution of other phase and combusted. In this research work, magneto – dielectric composite systems (30 wt % magnetic phase and 70 wt % dielectric phase) such as $CoFe_2O_4$ (CF)@$BaTiO_3$ (BT); $ZnFe_2O_4$ (ZF)@BT and $CoZnFe_2O_4$ (CZF)@BT have been prepared. Similarly, same weight percentage composites with interchanged phases (BT@CF, BT@ZF and BT@CZF) have also been prepared using above technique. All composite powders were calcined and the pellets were sintered at 1150 °C. XRD confirms the presence of dielectric and magnetic phases in the composites. FESEM images revealed plate-like along with nearly spherical morphologies of BT and polyhedral morphology of ferrite phase. Plate-like morphology was prominent in ferrite@BT composites, but suppressed when the phases were interchanged (i.e. BT@ferrite). The microstructural variation in the above composites led to change the magnetocapacitance response in both positive and negative directions, which is one of the novelty in the present composite systems. Further, magnetocapacitance response was analyzed using magneto-impedance results along with the help of Cole-Cole plots.

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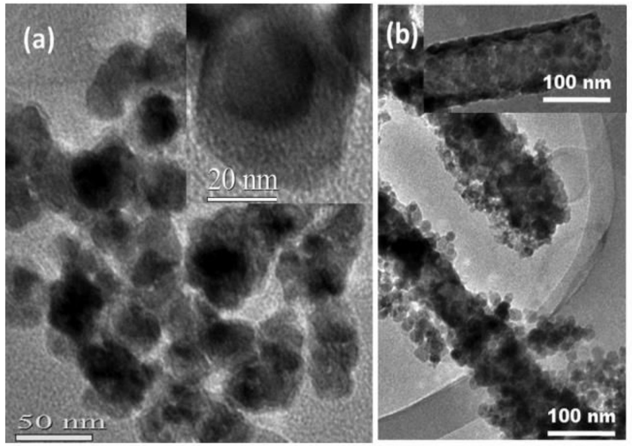
Magneto-capacitance

- ***A major property of magneto-dielectric composite materials.***
- $Magneto\ capacitance\ (MC)(\%) = \left\{\frac{\varepsilon\ (with\ H) - \varepsilon\ (without\ H)}{\varepsilon\ (without\ H)}\right\} X\ 100$
- ***Single phase compounds shows very low response (MC)***
- ***Research has been focused on the composite systems***
- ***Combination of piezoelectric (dielectric) and magnetostriction (ferrite) materials***
- ***Magnetostriction material gives strain on application of magnetic field and strain will polarize the piezoelectric material. This phenomena will led to show magneto-capacitance in magneto-dielectric composite systems.***
- ***Potential applications as sensors, actuators and devices.***

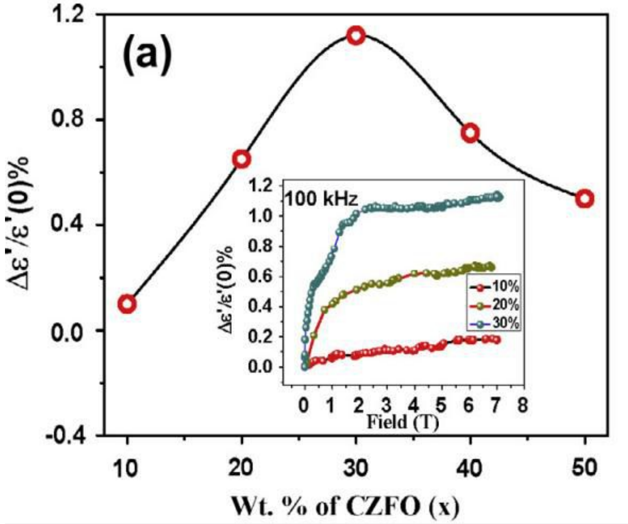
Factors that effect magneto capacitance response in magneto-dielectric composites

- ❑ **Intrinsic properties: Magnetostriction and Piezoeoelectric coefficients**
- ❑ **Extrinsic properties: Microstructure includes phase morphology and their connectivity and percentage of phase.**

“Magnetocapcitance being stress mediated phenomenon it demands large interface area among phases in any of the possible microstructural configuration depending on the percentage and morphology of phases”



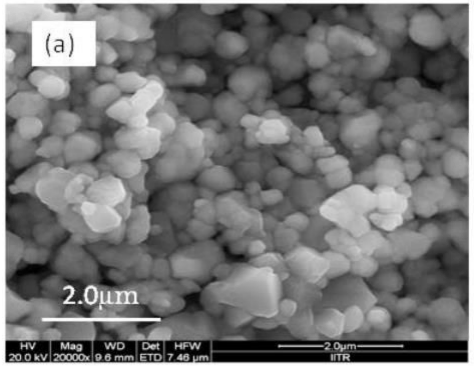
TEM images of CoFe2O4@BaTiO3 core-shell (a) nanoparticles and (b) nanotubes.
(Raidongia. K. et al. *APPLIED PHYSICS LETTERS 97, 062904 2010*)
4.7% change in MC in Nano tubes

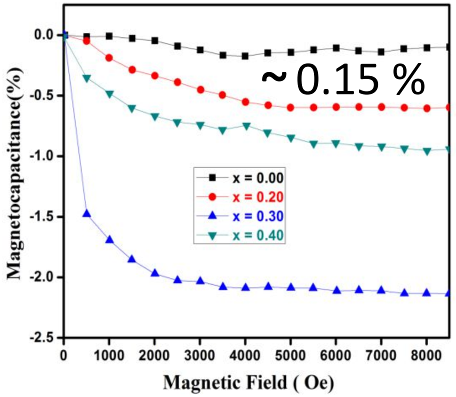


Percentage effect of ferrite on MC
(P.R. Mandal et al. *Journal of Alloys and Compounds 599 (2014) 71–77*)

Another example of microstructural Effect on MC in BT-ferrite composites

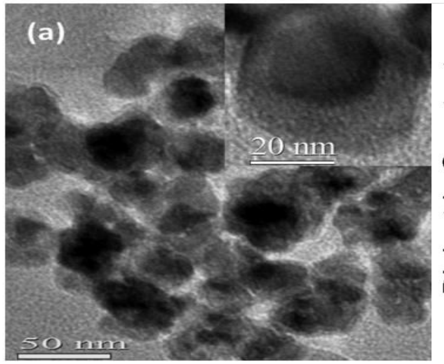
Particulate composite

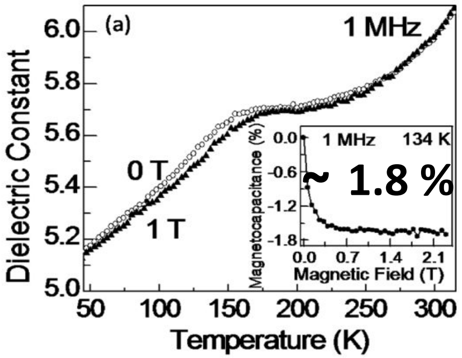




(Manjusha et al. Adv. Mat. Lett. 2014, 5(11), 652-657)

Core and shell particulate composite





(Raidongia. K . et al. APPLIED PHYSICS LETTERS 97, 062904 2010)

Requirements for enhancing or tuning MC

- **Larger interface area among the phases**
- **Nanocomposite systems**
- **Ferromagnetic phase should be isolated in the dielectric matrix of the composites to prevent the leakage currents**
- **Maximum density**
- **Tailoring microstructure using ex-situ derived wet-chemical methods**

OBJECTIVE

Tune the magneto capacitance response of the BT Ferrite composites (for fixed phase wt% of BT :Ferrite at 70:30)by tailoring the microstructure

HOW TO ACHIEVE OBJECTIVE

Using combustion synthesis technique

MATERIALS SYSTEMS

BT@CF	**BT@ZF**	**BT@CZF**
CF@BT	**ZF@BT**	**CZF@BT**

BT: $BaTiO_3$ CF:$CoFe_2O_4$ CZF: $CoZnFe_2O_4$

Combustion Synthesis of magneto-dielectric composites

Barium nitrate, Titanyl nitrate, citric acid, ammonium nitrate, EDTA in 1:1:1.5:12:0.1 wt ratio

↓

Dissolved in distilled water

↓

Under constant stirring ammonia was added to have pH ~7

↓

Ferrite powder based Solution left for an hour under constant stirring for homogeneity

↓

Increased temperature to 80 ^{o}C under constant stirring

↓

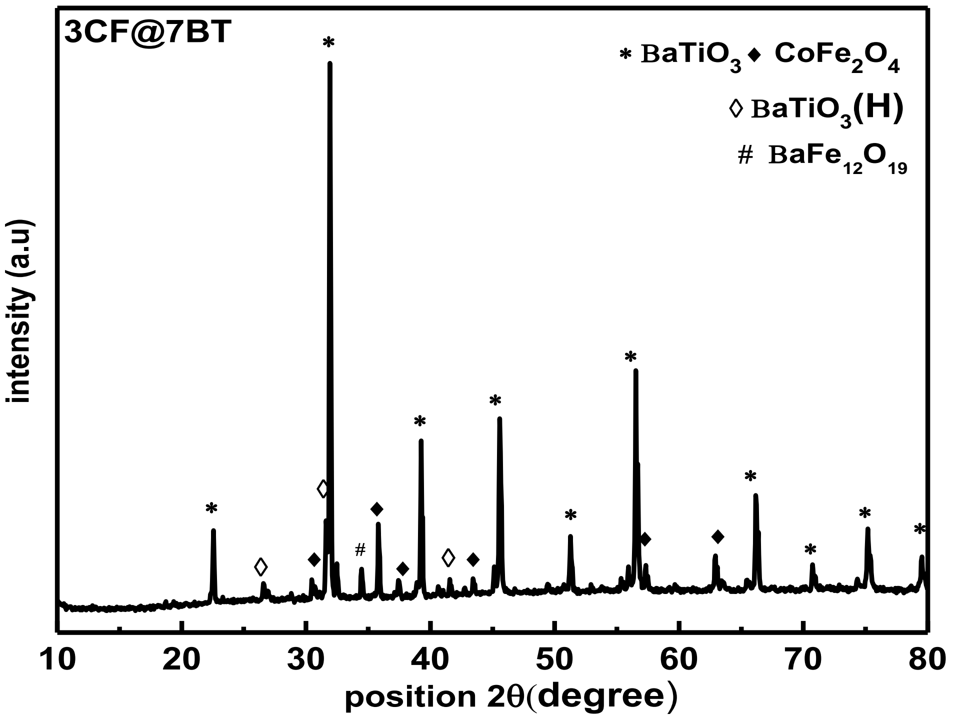
After water got evaporated, there was self ignition (leaving a fluffy mass)

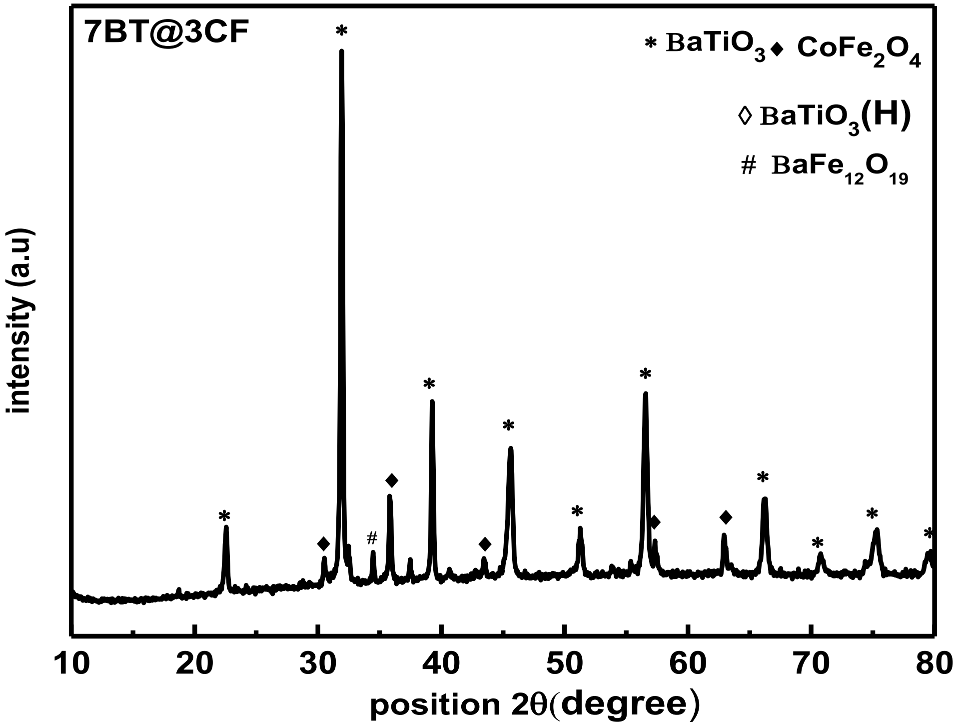
↓

Grinded powders were calcined at 800 ^{o}C for 4h and pellets sintered at 1150^{o}C for 6h

RESULTS AND DISCUSSION

XRD pattern of auto combustion derived Ex-situ magneto-dielectric composites





- **All the composite were identified with appropriate phases for composites like $BaTiO_3$ (tetragonal and hexagonal), $CoFe_2O_4$, $ZnFe_2O_4$ and $CoZnFe_2O_4$ (ferrites in cubic)**
- **Hexagonal Barium titanate ($BaTiO_3$ (H)) and Barium Hexa ferrite($BaFe_{12}O_{19}$) has been detected along with expected major phases.**
- **Hexagonal Barium titanate ($BaTiO_3$ (H)) was the result of oxygen vacancies due to substitution of low charged Fe^{2+}, Co^{2+} and Zn^{2+} ions in the place of high charged Ti^{4+} ions, which is prominent in ferrite@BT composites. [b, c]**
- **Barium Hexa ferrite($BaFe_{12}O_{19}$) was the result of diffusion of $Fe^{2+}$and Fe^{3+} ions in to the Ti^{3+} site, which is prominent in BT@Ferrite composites. [a, b]**

[a]K. Atchara et.al. Trans. NonFerrous Met. Soc. China 21(2011) 2438-2442. [b]H. Zheng et. al, Ceram. Int. 41 (2015) 1511–151. [C]H.Zeng et.al. J. Appl. Phys. 113 (2013) 044101.

FESEM micrographs of auto combustion derived Ex-situ magneto-dielectric composites having different ferrites ($CoFe_2O_4$ (CF), $ZnFe_2O_4$(ZF)and $CoZnFe_2O_4$ (ZCF))

- Ex-situ Synthesis method has an high impact on microstructure which shows rich diversity in it.

- Ferrite@BT composites shows the plate like BT phase erupted out of surface and suppressed the ferrite phase.

- Similarly ferrite mostly appears on surface BT@ferrite composites.

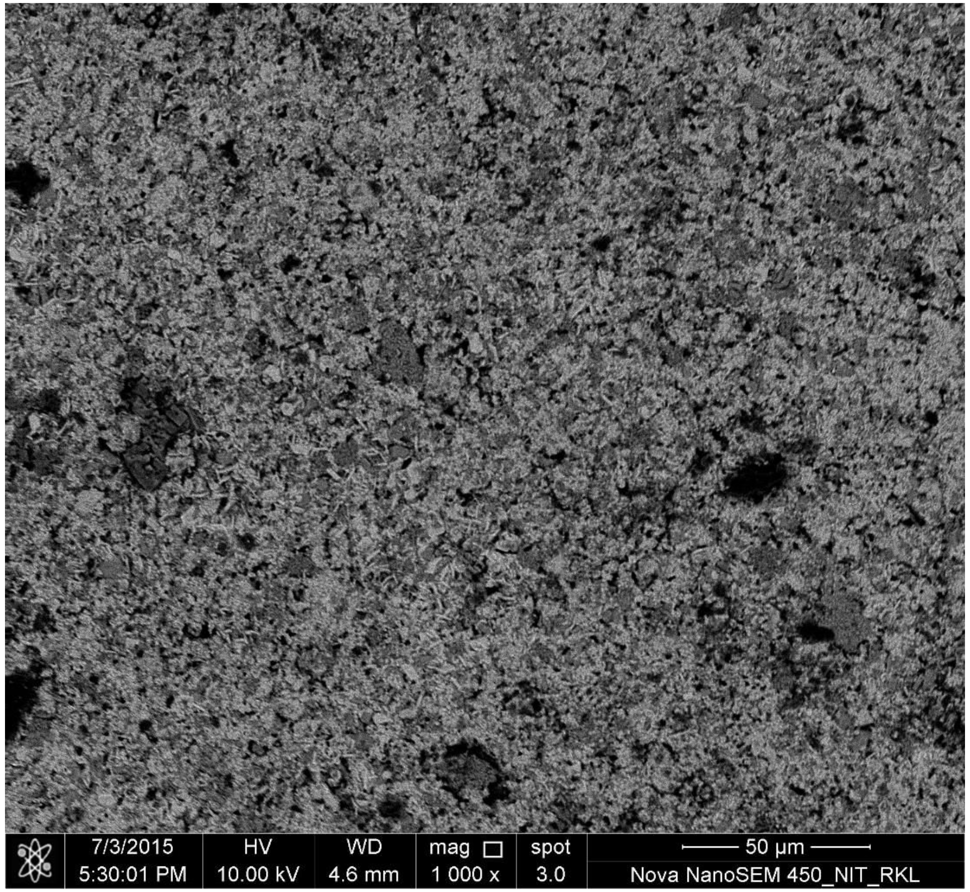
- Also composites densities are also varied much with the method of synthesis, which ferrite@BT composites has higher densities than BT@Ferrite

- Plate like BT may have impact on the packing of the composites

- Ferrite found in polyhedral morphology.

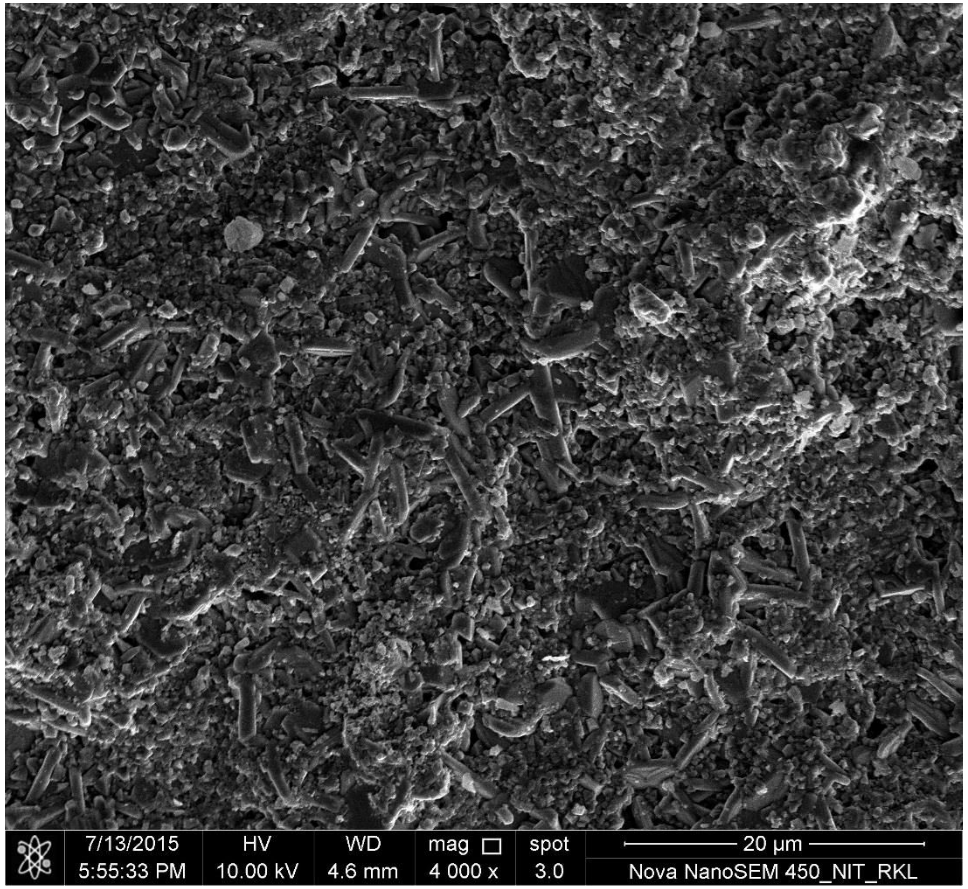
Micrograph of BT-CF composites

CF@BT

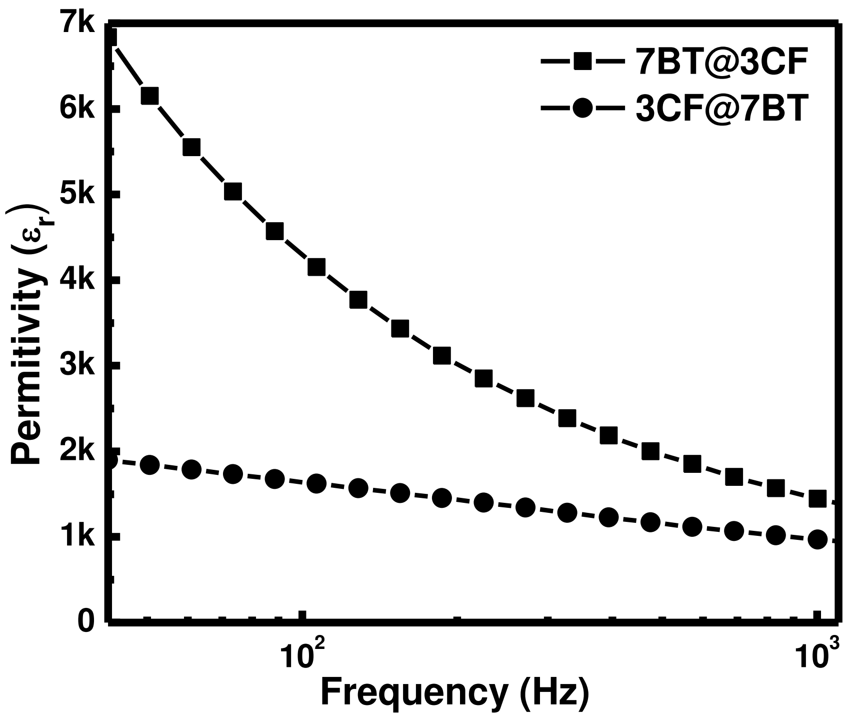


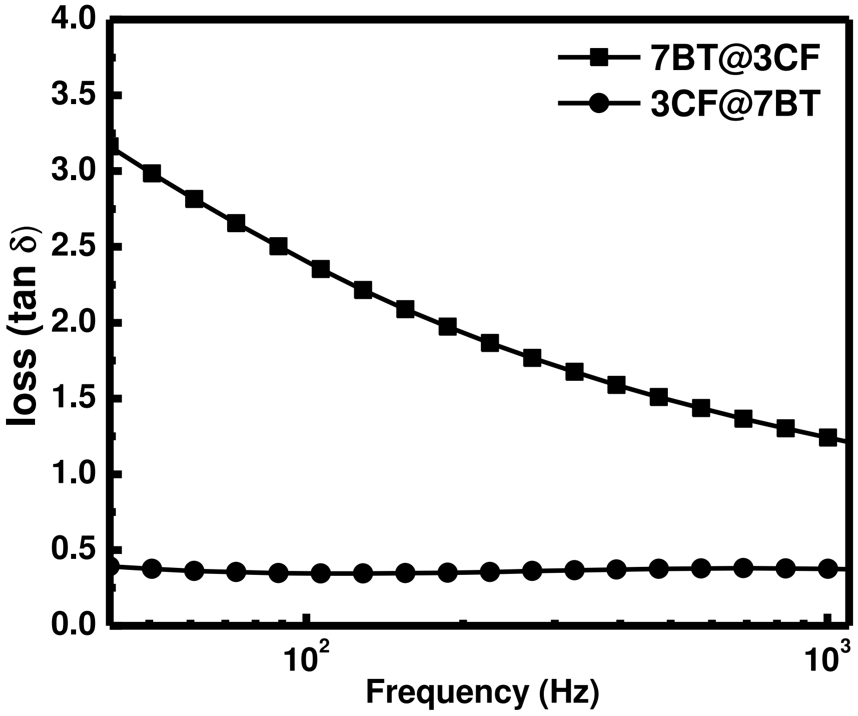
Micrograph of BT-ZF composites

ZF@BT



Dielectric properties of auto combustion derived Ex-situ magneto-dielectric composites

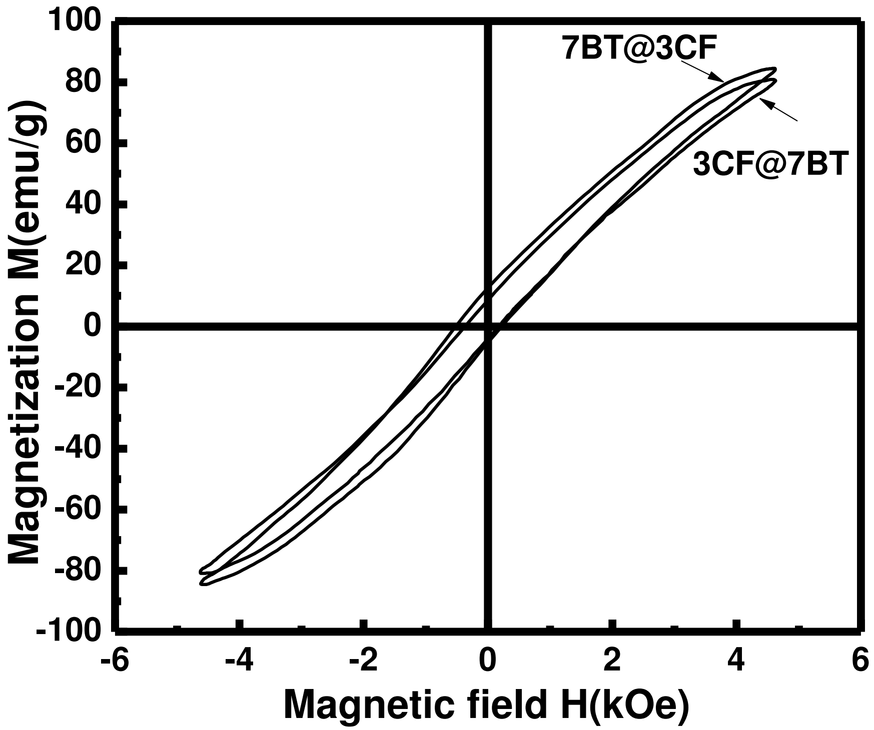




- **Sharp fall in permittivity near the lower frequency is due to Maxwell-wagner interfacial polarization among the plate like BT and ferrite phase particularly in the BT@ferrite composites.** [a,b,c, d and e]
- **Similarly loss behavior due to connective conductive ferrite phase which covers the BT, and can be observed from the tan(δ) with respective frequency.**
- **Zinc ferrite based composite has lower loss compare to other composites, which is purely microstructural effect, than intrinsic.**

[a]H. Zheng et. al, Ceram. Int. 41 (2015) 1511–151. [b]H.Zeng et.al. J. Appl. Phys. 113 (2013) 044101. [c]M. Rafiquea et.al. Ceram. Int, 39 (2013) S213–S216. [d]L. Mitoseriu et.al.J. Mag. Mag. Mat. 316 (2007) e603-e606. [e]H. Yang et.al Mater. Chem. Phys. 134 (2012) 777-782

M-H loop behavior of auto combustion derived Ex-situ magneto-dielectric composites



- **Polarization in the composites shows the lossy capacitor behavior due to ferrite (hopping between Fe^{2+} and Fe^{3+}) phase, how ever BT@ferrite composites has the more loss compared to ferrite@BT.** [a and b]
- **Cobalt and cobalt zinc ferrite composites show the magnetic behavior in MH loop, but zinc ferrite composites has no magnetic behavior like others.**

[a]K. Atchara et.al. Trans. NonFerrous Met. Soc. China 21(2011) 2438-2442. [b]H. Zheng et. al, Ceram. Int. 41 (2015) 1511–151

Magneto capacitance values of auto combustion derived Ex-situ magneto-dielectric composites having different ferrites ($CoFe_2O_4$ (CF), $ZnFe_2O_4$(ZF)and $CoZnFe_2O_4$ (ZCF))

	BT@CF	CF@BT	BT@ZF	ZF@BT	BT@CZF	CZF@BT
0.5 k Oe	2.9	-5	2.8	-1.6	0.007	1.81
1 k Oe	0.14	-6.24	7	-2.1	0.67	2.9
2 k Oe	6.21	-6.05	14.2	-2.3	6	4.7

Table shows the magneto capacitance values (in %) for composites at different magnetic fields

- **Cobalt zinc based compotes has the field dependent MC in both BT@CZF and CZF@BT.**
- **But in Cobalt ferrite and Zinc ferrite composites particularly ferrite@BT shows the saturation (at 1 kOe) behavior with little MC comparatively**
- **MC behavior in CZF ferrite composites increasing in nearly exponential (prominent in BT@CZF) at higher fields in positive sign.**
- **How ever cobalt ferrite and zinc ferrite composites shows the both positive (BT@ferrite) and negative (ferrite@BT) MC behavior which can distractive depend on synthesis method**

Magneto impedance (at 2.68 kOe) of auto combustion derived Ex-situ magneto-dielectric composites having different ferrites ($CoFe_2O_4$ (CF), $ZnFe_2O_4$(ZF)and $CoZnFe_2O_4$ (ZCF)) at different frequencies

	BT@CF	CF@BT	BT@ZF	ZF@BT	BT@CZF	CZF@BT
1 K	-3.45	13	0.01	6.9	334	51
100 k	11.14	-1.8	58	-3.08	110	25
1 M	16	5.6	43	-6.63	27	25

Table shows the magneto impedance data fro composites at different frequencies

Mostly frequency independent

- **Magneto impedance (MI) data of magneto dielectric composites has the unique information regarding MC origins**
- **Frequency dependent behavior comes from the MR of material which is intrinsic**
- **Frequency independent MI has the origins from the Magnetostriction**

Partially frequency dependent

- **Cobalt ferrite and Zinc ferrite composites shows the less MR effect contribution in the MC effect**
- **Where as cobalt zinc ferrite composite having BT@CZF morphology has the most of its MC response from the MR**
- **Microstructure influence is huge in BT-CZF ferrites.**

conclusions

- **Magneto dielectric Composites have been synthesized successfully using Ex-situ solution combustion synthesis technique.**
- **Ex-situ synthesis method plays an important role in tuning the microstructure as well as modifying the magneto-dielectric properties.**
- **Comparatively, stress induced MC was observed in cobalt ferrite composite.**
- **Both positive and negative magneto-capacitance response has been observed in both cobalt and zinc-ferrite composites due to strong microstructural effect.**
- **Ex-situ derived combustion synthesis method has wide range of opportunities to tune MC, MR and MI for building up devices.**

Thank you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