Microstructure effect on the structural, interfacial and magnetic properties of particulate composite and 0-3 core shell composite

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Abstract. The microstructure of the particulate composite vs. 0-3 core shell composite has a noticeable effect on the structural, interfacial and magnetic properties. Both particulate composite and 0-3 core shell composite have the same components. X-ray diffraction has been used for all samples to identify the structural properties. The microstructures have been investigated by TEM and particle size distribution was calculated. By using IR Spectroscopy, vibrational bands have been exploited to recognize the interfacial interaction. Magnetic hysteresis curves have been measured by VSM. The relative permeability vs. temperature experiment have been measured and Curie temperatures have been determined.

1. Introduction

Nanosized spinel ferrite particles have attracted much attention in recent years because of their potential applications in high density magnetic recording, magnetic fluids, spintronics, data storage and gas sensors [1, 2]. Among the ferrite nanoparticles, Co-, Ni-, Co-Ni- ferrites have been widely studied due to their excellent chemical stability, reasonable saturation magnetizations and high saturation magnetostriction constants. These properties make them promising candidates for many applications, such as magnetic data storage, magnetic drug targeting, biosensors and magnetic refrigeration [3,4].

Lead zirconate-titanate PbZr0.52Ti0.48O3 (PZT) is a commonly used material in its ceramic form, used in a wide variety of technological applications. It has a perovskite structure and has a particular interest due to its high piezoelectric and pyroelectric properties [5]. The crystal structure of PZT, at composition x~0.48 which is known as the morphotropic phase boundary (MPB), is tetragonal [6].

Magnetoelectric multiphase multiferroic materials have drawn increasing interest due to their potential for applications as multifunctional devices. Magnetoelectric (ME) coupling ‘effect’ in ferroelectric-ferrimagnetic composites depends on the efficiency of strain transfer across the interface and requires a strong inter-phase elastic interaction. The inter-phase is determined directly by the synthesizing technique that defines the way that the two phases can interact. For instance, particulate, (0-3) core shell and layered (2-1, 2-2) ME composites that have been reported in previous literatures extensively to provide varying range of coupling (or ME effect) by tailoring the magnitude of strain [7]. Consequently, the studying of microstructure and its effect on structural and magnetic properties, and investigating about the interface interaction is crucial for recognizing the ME effect in these materials.

In this paper, the effect of microstructure on the structural, vibrational and magnetic properties of 0-3 core shell (C.S.) and particulate composite (composite) have been studied. Both types of composites contains 40% of Co1-xNixFe2O4 (x=0.0 (CFT), 0.9 (CNFT), 1.0 (NFT)) ferrites were added to 60% of PbZr0.52Ti0.48O3 (PZT). The samples were classified into three groups and were assigned by the name of the ferrite candidate, for example, CFT group that contains CFT, PZT, CFT+PZT composite and
CFT+PZT C.S., and the same for CNFT group and NFT group. It was found that the three groups behaved likely for the effect of microstructure on structural, vibrational and magnetic properties. Hence, we will introduce CFT group only as an example. All samples are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), IR spectroscopy and magnetic properties were studied.

2. Experimental techniques.

2.1. Synthesizing techniques.

2.1.1. CoFe$_2$O$_4$ (CFT) synthesizing.
The spinel ferrite of compositions (CoFe$_2$O$_4$) was prepared by sol-gel auto combustion method as previously reported [8]. Analytical grade of cobalt nitrate (Co(NO$_3$)$_2$.6H$_2$O) and ferric nitrate (Fe(NO$_3$)$_3$.9H$_2$O) were taken in stoichiometric proportion with citric acid and were dissolved in deionized water. This reaction yields the as prepared nanoferrite powders with relatively high hematite foreign phase. CFT powder was annealed at 600°C, for 2h with heating rate 4°C/min to get rid of the hematite phase. The obtained single phase powder was divided into three equal amounts. One part was used to study the ferrite alone and the others were used in synthesizing composite and C.S.

2.1.2. PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT) synthesizing.
The tetragonal phase with composition PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT) was synthesized by hydrothermal method to get monodisperse and low nanosize particles [9]. Zirconium (IV) oxynitrate hydrate and lead nitrate were mixed together in 20 ml distilled water and then poured in a 100 ml Teflon tube that is especially designed for autoclave reactor. Then Titanium isopropoxide was syringed in this solution without exposing to air and then stirred for 20 min. Potassium hydroxide KOH as a mineralizer solution was then added on the wall of the Teflon tube under gentle stirring to adjust the PH at 14 (extreme alkaline solution) such that the total volume in the Teflon tube was around 70 ml. Then the Teflon tube was putted in the hydrothermal autoclave reactor and firmly closed. The reactor was annealed at 200°C for 120 min. Then, the precipitates were filtered, washed with distilled water to remove the soluble nitrates and dried in air at 110°C. The obtained powder was single phase and did not need to any further heat treatment.

2.1.3. Particulate Composites (Composite) synthesizing.
Single phase of PZT and CFT powders were milled together for two hours by using Agate Mortar Grinder Mill RM100. The ratio of mixing between the ferrite and ferroelectric was kept to be 40% ferrite: 60% PZT. The obtained powders were annealed at 600°C, for 2h with heating rate 4°C/min.

2.1.4. (0-3) Core shell Composites (C.S.) synthesizing.
The preparation of C.S. will be implemented in two steps: First step is concerned with CFT ‘core’ surface modification. The single phase CFT was mixed with Oleic acid in presence of NaOH [10]. The mixture was sonicated, washed and filtered to get surface modified ferrites. Second step is about the PZT ‘shell’ formation. Glacial acetic acid was added to the mixture of citric acid + Pb Nitrate + Zr – Oxy Nitrate hydrate. The solution was heated under stirring at 80°C and then Ti-iso propoxide was syringed in the solution. The modified ferrite was added to the previous solution and then ethylene glycol was added to promote the gel formation. The solution was kept at 80°C with continuous stirring over night until the powder dried completely. The obtained powders were annealed at 600°C, for 2h with heating rate 4°C/min [11].

2.2. Characterizations and Measurements.
XRD patterns were recorded by Malvern Panalytical device with Cu-Kα radiation. The d$_{hkl}$-spacing for each peak was recorded automatically and then the lattice parameter (a) was calculated by using the method of extrapolating function of Nilson-Riley. Size-Strain analysis has been done by using XRD built in program called “HIGH SCORE PLUS” program. TEM images were captured and selected area of electron diffraction (SAED) was chosen by JEOL 1200ex2 transmission electron microscope. IR charts
were obtained from Bruker MPII FTIR spectrometer. Vibrating sample magnetometer (VSM) was used to get M-H hysteresis curves at room temperature. Relative permeability and Curie temperature were determined by induction method employing RLC Bridge.

3. Results and discussion.

3.1. Structural and Microstructural studies

Figure 1 shows XRD patterns for CFT group candidates. It is clear from Figure 1 that the CFT and PZT show single phase patterns with cubic (Fd3m) and tetragonal (P4mm) structures respectively. Composite and C.S. show double phase of ferrite and PZT together. Moreover, the intensity of peaks for PZT is larger than for CFT in composite and C.S. which is compatible with the synthesizing condition (60% PZT: 40% ferrite).

![XRD patterns for CFT group candidates](image)

Figure 1. XRD patterns for CFT group candidates.

Table 1 records the microstrain, CFT lattice parameter, PZT tetragonality degree and crystallite size for each candidate in CFT group.

| Sample Name    | Lattice Parameters (Å) | (c/a)     | Strain (%) | XRD Size (nm) |
|----------------|------------------------|-----------|------------|---------------|
|                | Ferrite | PZT |     | Ferrite | PZT | Ferrite | PZT |
| CFT            | 8.382    |     |     | --- | 22 | --- | --- |
| PZT            | --- | 4.041 | 4.129 | 1.022 | --- | 0.490 | --- | 9 |
| CFT+PZT Composite | 8.385 | 4.014 | 4.049 | 1.009 | 0.306 | 0.791 | 42 | 18 |
Table 1 show that the microstrain of CFT increased either in composite or in C.S. On the other hand, the microstrain of PZT increased in composite but decreased in C.S. The increase of microstrain in composite is due to what is called ‘mutual microstrain’ which results from the crystal growth of the two phases simultaneously. The increase of microstrain of CFT in C.S is due to the increase of pressure of PZT on CFT. However, the decrease of microstrain of PZT in C.S is due to the fact that most of the supplied energy is consumed in formation of PZT and not in crystal growth.

Lattice parameters show distinct behaviors in ferrite rather than PZT, as shown in table 1. The lattice parameter for CFT displays nearly constant behavior. This constancy is due to the absence of the parameters that affects on the lattice parameters such as macrostrain “uniform strain’ and changing of the crystal structure [12]. Contrary, tetragonally degree (c/a) of PZT shows a noticeable decrease. The decrease of this parameter from PZT single to composite may be attributed to two reasons. First, it is well known that PZT structure transfers from tetragonal to cubic when it is exposed to a temperature (T_{annealing} = 600°C) higher than its Curie temperature (T_C =400°C). Thus transformation is accompanied by a decrease in c/a [6]. Second, the volatility of Pb ion during heating of composite causes A-site vacancy in the pervoskite ABO_3 structure. This vacancy makes shrinkage of the unit cell that decreases c/a value [6]. On the other hand, the tetragonally degree (c/a) of PZT in C.S. is slightly larger than that of composite. This is due to that the PZT was formed for the first time over the ferrite seeds. So their values are close to the original values of PZT single.

Table 1 indicates to that the crystallite size of CFT increased in composite then decreased in C.S. The increase of the size in case of composite is due to the crystal growth while the decrease in size may be attributed to the inhibition of the crystal growth as PZT particles surround the CFT [14]. While, the increasing of PZT crystallite size with temperature shows a normal behavior due to crystal growth effect.

Figure 2 (a-d) shows the TEM images and selected area of electron diffraction (SAED) of composite and C.S. samples in CFT group. Also, figure 2 (e, f) shows the histograms of ferrite in these samples that is used to declare the particle size distribution and to calculate the mean TEM size.
Figure 2. (a), (b) TEM images, (c), (d) SAED’s and (e), (f) Histogram for particle size distribution for CFT C.S. and Composite respectively.

From figure 2 (a) and (b), we can distinguish between the microstructure of composite and C.S. Also, PZT and CFT particles could be identified through the difference in transmission intensities between them. Moreover, the interface between the CFT ‘core’ and PZT ‘shell’ in figure 2 (a) is easily identified in C.S. that is a proof of well interaction between the two phases which is a promising property in ME applications. However, figure 2 (b) shows poor interaction between PZT and CFT particles. The SAED patterns in figure 2 (c) and (d) confirm that both CFT and PZT phases exist in composites and C.S. without additional traces of other phases which confirm the results of XRD. Histograms of CFT in C.S. and composite show a narrow distribution of the particle size, as shown in figure 2 (e) and (f). This indicates to that the preparation of sol-gel is a suitable technique for synthesizing nanoferrite material with narrow distribution. Also, the mean particle sizes of ferrites in composite and C.S. are very close to crystallite sizes calculated from XRD, Table 1.
3.2. IR vibrational study

It is known that IR is a powerful tool for structural analysis of single phase or composite. It can be utilized in investigations of presence of the interface interactions between the multiphases constitutes. This could be recognized through appearing of new bands or shoulders in IR spectrum. These new bands or shoulders are obtained as result of new localized bonds between the two phases [15]. In this paper IR spectroscopy was used to investigate the structural and interfacial properties of CFT group. IR spectrum of CFT group is shown in figure 3 (a-d). Ferrites have four characteristic wave numbers $\nu_1$ (around 600 cm$^{-1}$) for tetrahedral local symmetry cations, $\nu_2$, $\nu_3$, (around 300 cm$^{-1}$) for octahedral local symmetry cations and $\nu_4$ (around 200 cm$^{-1}$) for lattice vibrations. As shown in figure 3 (a) for CFT, there is a band at (580 cm$^{-1}$) that assigned for Fe$^{3+}$ -O in tetrahedral position. Also, there is a band at (325 cm$^{-1}$) and two shoulders at (383, 369 cm$^{-1}$) that assigned respectively for Co$^{2+}$ -O, Fe$^{3+}$ -O and Fe$^{2+}$ -O vibrations in octahedral site [16]. These results suggest that the cation distribution is inverse ferrite and confirm the presence of Fe$^{2+}$ but with small amount. Finally, for the lattice vibration, we can assign the band (282 cm$^{-1}$) [8].

PZT has only octahedral site as a local symmetry with off-center B-atom in the distorted pervoskite structure ABO$_3$ [6]. All characteristic bands and shoulders for PZT appear in our result. As shown in figure 3 (d), there are two overlapped bands with asymmetric minimum at (599 cm$^{-1}$) that assigned for stretching modes for Zr-O and Ti-O [17]. Also, the bending mode of the octahedral site for Zr-O and Ti-O are observed in small shoulders at (362 cm$^{-1}$, 354 cm$^{-1}$, 316 cm$^{-1}$, 301 cm$^{-1}$). Finally, the octahedral lattice vibration (BO$_3$)$^{2-}$; B: octahedral cation and O: oxygen anion, are noticed at (280 cm$^{-1}$) [18]. Two bands appeared at (241 cm$^{-1}$, 232 cm$^{-1}$) due to the modified phonon-phonon interaction evolved from the nanosize quantum confinement [19] and the appearance of surface phonon modes [20].

In composite and C.S., it was expected that the appeared number of bands and shoulders might increase but actually they decreased. Also, in C.S. there is a broader band rather than composite as shown in figure 3 (c, d) and most of the apparent bands are located in between the bands of PZT and CFT. The broadening may reflect the presence of large overlapped vibration modes. Generally in composites the presence of new bands or shoulders depends on the extent of the heterogeneous interaction. This heterogeneous interaction forms what is called interface localized bonds. So, according to figure 2 (a,b) it is obvious that the probability of presence of interface localized bonds in C.S. is larger than in composite.

3.3. Magnetic Studies
Magnetic hysteresis (M-H) curves and the relation of relative permeability vs. temperature ($\mu_r$-T) for CFT group are shown in figure 4 (a) and (b). Curie temperatures are obtained from the intersection of the curve of ($\mu_r$-T) with the temperature axis, figure 4 (b).

It is clear from figure 4 (a) that the saturation magnetization $M_s$, remanence magnetization $M_r$ and coercivity $H_c$ are greater in CFT than C.S. and composite. This is because that C.S. and composite samples contain 60% PZT ‘non-magnetic material’ that decreases the values of magnetic hysteresis parameters. Also, $M_s$ and $M_r$ are larger in C.S. than composite, while $H_c$ has an opposite trend. The increase of the parameters of $M_s$ and $M_r$ in C.S. in comparing with composite is attributed to the increase of the mutual microstrain in C.S. rather than composite due to the distinct microstructure of C.S., as we mentioned in sec 3.1. The relation between mutual microstrain and the magnetic properties could be explained in the light of inverse magnetostriction effect. This effect means that the magnetic parameters $M_s$ and $M_r$ in addition to $\mu_r$ increase due to applying stress that yield strain, either microstrain ‘nonuniform strain’ or macrostrain ‘uniform strain’. Knowing, this effect works only with magnetic materials that have –ve magnetostriction coefficients such as CFT. This attribution was confirmed from figure 4 (b) since room temperature $\mu_r$ of C.S. was found to be larger than composite sample as it was expected. On the other hand, $H_c$ behavior in CFT, C.S. and composite could be easily realized through the inverse relation between $H_c$ and $\mu_r$ [3], as could be noted from figure 4 (a) and (b). Hence, the microstructure apparently modified the magnetic parameters ($M_s$, $M_r$ and $\mu_r$) and make the C.S. material could be easily switchable with magnetic field and produces higher $M_s$ rather than composite. This enhancement was expected to increase the ME coefficient that could be utilized in magnetoelectric random access memory (MeRAM) [21].

On the other hand, as mentioned in figure 4 (b), Curie temperature in CFT is less than those of C.S. and composite. This is also due to the effect of microstructure that yields mutual microstrain in C.S. and composite greater than CFT single. Consequently, the mutual microstrain hinders the moments to fluctuate under the thermal effect. So to overcome this hindering and to convert to paramagnetic state (complete thermally fluctuating moments), more thermal energy is needed. Therefore, the microstructure affects positively on the Curie temperature and increases the thermal stability of the CFT material.

4. Conclusion
The microstructure of composites has a significant influence on the structural, vibrational and magnetic properties. The ferrite candidates $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x=0.0, 0.9, 1.0$) (CFT, CNFT, NFT) and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) were synthesized successfully by using sol-gel and hydrothermal techniques respectively. Then CFT, CNFT, NFT ferrites were added to PZT to form particulate composite (composite) and was introduced to act like seeds in 0-3 core shell composite (C.S.) such that C.S. and composite have different microstructure. So, three groups were formed and named according to the ferrite candidate such that (CFT, PZT, CFT-PZT particulate composite and CFT-PZT 0-3 core shell composite) called CFT group and the same for CNFT group and NFT group. The results of these groups behave likely, so CFT group was only included as an example. XRD was performed to all the samples in the CFT group that confirms the formation of PZT and CFT in either in single form or as a composite and C.S. The mutual microstrain between PZT and CFT was large in C.S. in comparison with composite due to the unique microstructure of C.S. Also, the microstructure affected on the size of ferrite during the thermal treatment, such that the size of ferrite in C.S. was 22nm while in composite was 42nm. The lattice parameter and tetragonality degree of PZT was obviously affected by the microstructure of composite. TEM images declared the distinct microstructure of C.S. rather than composite. The average particle size was compatible with XRD size. SAED was performed to confirm the results of XRD and to ensure from absence of foreign phases. Histograms proved that the microstructure affects on the particle size distribution such that the particle size distribution was narrow in case of C.S. due to the effect of PZT shielding. The microstructure affected on the number of bands appeared on the IR spectrum and show a broad band in C.S. rather than composite that might be due to the presence of interface localized bonds that create additional bands. So, these localized bonds are clue for elevation of interface interaction and consequently the “mutual microstrain” in C.S. will be large in comparison with composite. Saturation magnetization, remainance and permeability increased in C.S., while coercivity decreased. This is due to the effect of mutual microstrain that enhanced the converse magnetostrictive effect which increases the saturation, remainance and permeability and decreases the coercivity by strain (either microstrain or macrostrain). Curie temperature of CFT was remarkably increased in C.S. and composite due to the increment of mutual microstrain that hinders the magnetic moment fluctuations. In conclusion, the microstructure affects on different properties through the mutual microstrain parameter.

References

[1] Veena Gopalan E, Joy P A, Al-Omari I A, Sakthi Kumar D, Yasuhiko Yoshida and Anantharaman M R 2009 J. All. Comp. 485 711.
[2] Mathew George, Asha Mary John, Swapna S Nair, Joy P A and Anantharaman M R 2006 J Magn. Magn. Mater. 302 190.
[3] Cullity B D and Graham C D 2009 Introduction to Magnetic Materials (New Jersey: John Wiley & Sons Inc.) chapter 8 p 251.
[4] Zhenfa Zi, Yuping Sun, Xuebin Zhu and Wenhai Song 2009 J Magn. Magn. Mater. 321 1251.
[5] Yokota H, Zhang N, Taylor A E, Thomas P A and Glazer A M 2009 Phys. Rev. B 80 104109.
[6] Jaffe B and Cook W R et al. 1971 Piezoelectric Ceramics (London: Academic Press) p 200.
[7] Manfred Fiebig and Victor V Eremenko et al. 2003 Magnetoelastic Interaction Phenomena in Crystals (Sudak, Ukraine: Springer – Science +Business Media) p 110.
[8] Agami W R, Ashmawy M A and Satarr A A 2013 J Mater. Eng. and Perform 23 604.
[9] Roxana M, Piticescu R R, Taloi1 D and Badilika V 2003 Nanotechnology 14 312.
[10] Corral-Flores V, Bueno – Baque’s D and Ziolo R F 2016 Acta Materialia 58 764.
[11] Gollapudi Sreenivasulu, Maksym Popov, Ferman A Chavez, Sean L Hamilton, Piper R Lehto and Gopalan 2014 App. Phys. Lett. 104 052901.
[12] Cullity B D and Stock S R 2014 Elements of X-Ray Diffraction (Edinburgh: Pearson Education
Limited) p 406.

[13] Kalyan Raidongia, Angshuman Nag, Sundaresan A and Rao C N R 2010 *App. Phys. Lett.* 97 062904.

[14] Araújo E B, Yukimitu K, Moraes J C S, Pelaio L H Z and Eiras J A 2002 *J Phys. Condens. Matter* 14 5195.

[15] Henriksson A and Hoffmann H 2012 *App. Spectro.* 66 1320.

[16] Waldron R D 1955 *Phys. Rev.* 99 6.

[17] Araújo E B, Guarany C, Yukimitu K, Moraes J C S and Eiras J 2006 *Ferroelectrics* 337 145.

[18] Last J T 1957 *Phys. Rev.* 105 6.

[19] Arora A K, Rajalakshmi M, Ravindran T R and Sivasubramanian V 2007 *J. Raman Spectrosc.* 38 604.

[20] Sahoo Satyaprakash, Hu M S, Hsu C W, Wu C T, Chen K H, Chen L C, Arora A K and Dhara S 2008 *App. Phys. Lett.* 93 233116.

[21] Kang L Wang, Hochul Lee and Pedram Khalili Amiri 2015 *IEEE Trans. on Nanotech.* 14 992