Division of Materials Sciences and Engineering

Office of Basic Energy Sciences

US Department of Energy

1. DOE award # and name of the recipient (Institution)

DE-FG02-06ER46288

The University of Texas Arlington

2. Project Title and name of the PI

Mesoscale Interfacial Dynamics in Magnetoelectric Nanocomposites

Shashank Priya (PI)

3. Date of the report and period covered by the report

March 22, 2007

August 2006 – March 2007

4. A brief description of accomplishments. This can be in bullet form or whatever you think is useful and appropriate to indicate the sense of progress. Please limit this section to no more than 5 pages.

The last eight months of our study was focused on synthesizing the nanocomposites using controlled precipitation method to obtain interfaces with varying degree of crystallography. The characterization of the synthesized composites will provide interfacial structural, electrical and magnetic response which will be used for understanding the fundamental process occurring under the electric and magnetic fields and also used for the phase field modeling at Rutgers University. XRD, TEM, and ME characterization of the samples was done at UTA while PFM analysis was done at VT.

The controlled precipitation process was designed to take advantage of the temperature and time dependence of the phase distribution and strain relaxation allowing control of the magnetic and ferroelectric domain size and orientation. Initially, we applied this method to study the changes in the PZT – NFM (Nickel Ferrite) system in terms of (i) bulk magnetoelectric response, (ii) domain structure, and (iii) elastic strain fields. The process consists of three-step heat treatments: solid solution heat treatment, unidirectional cooling, and aging. Reagent-grade oxides in stoichiometric ratios corresponding to composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) and $NiFe_{1.9}Mn_{0.1}O_4$ (NFM) were used for processing using the mixed oxide route. Pressureless sintering of composites was performed in air using a high temperature vertical gradient furnace in the temperature range of 1150^{o}C for 2 hours followed by quenching. The thermal treatment on the sintered samples constituted of annealing at 800^{o}C for 10 hours followed by rapid air cooling and aging at 300^{o}C for 5 hours.

Another objective of this study was to confirm the hypothesis that elastic coupling can be maximized by having coherent response from the magnetostrictive phases such that the stress on the piezoelectric lattice is in phase with each other. The in-phase response implies that the stress terms arising from magnetostrictive phases adds together rather than being averaged out in the grain. Figure 1 shows the TEM structure of the as – sintered, annealed and aged specimens.

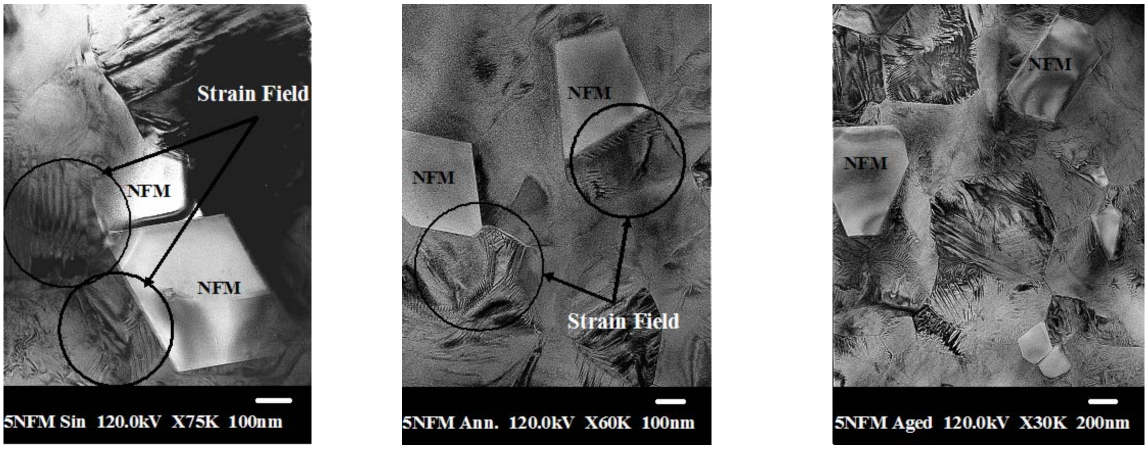

Figure 1: TEM micrographs of the PZT – NFM specimens, (i) as-sintered, (ii) annealed, and (iii) aged states. Significant changes in the magnitude of the strain fields present at the piezoelectric – magnetostrictive interface can be seen by comparing the three micrographs.

The structural analysis of the microstructures is still in progress. However, preliminary calculations shown in Fig. 2 on the PZT – NFM grains indicate that relaxation in the lattice strain during the aging process enhances the elastic coupling between the piezoelectric and magnetostrictive phases. The lattice parameters calculated from the spot diffraction pattern for the sintered composition were found to be as: <u>PZT phase</u> (a = 4.058 Ǻ, c = 4.132 Ǻ, c/a = 1.0182), while <u>NFM Phase:</u> (a = 8.42 Ǻ). The lattice parameters for the annealed ad aged samples were found to be as: <u>PZT phase</u> (a = 4.048 Ǻ, c = 4.154 Ǻ, c/a = 1.026), while <u>NFM Phase:</u> (a = 8.41 Ǻ). There is very little change in the NFM phase constants but a significant change occurs in the tetragonality of the PZT phase. At this point we are expecting this change is correlated to the relaxation in the strain fields but more accurate analysis is required.

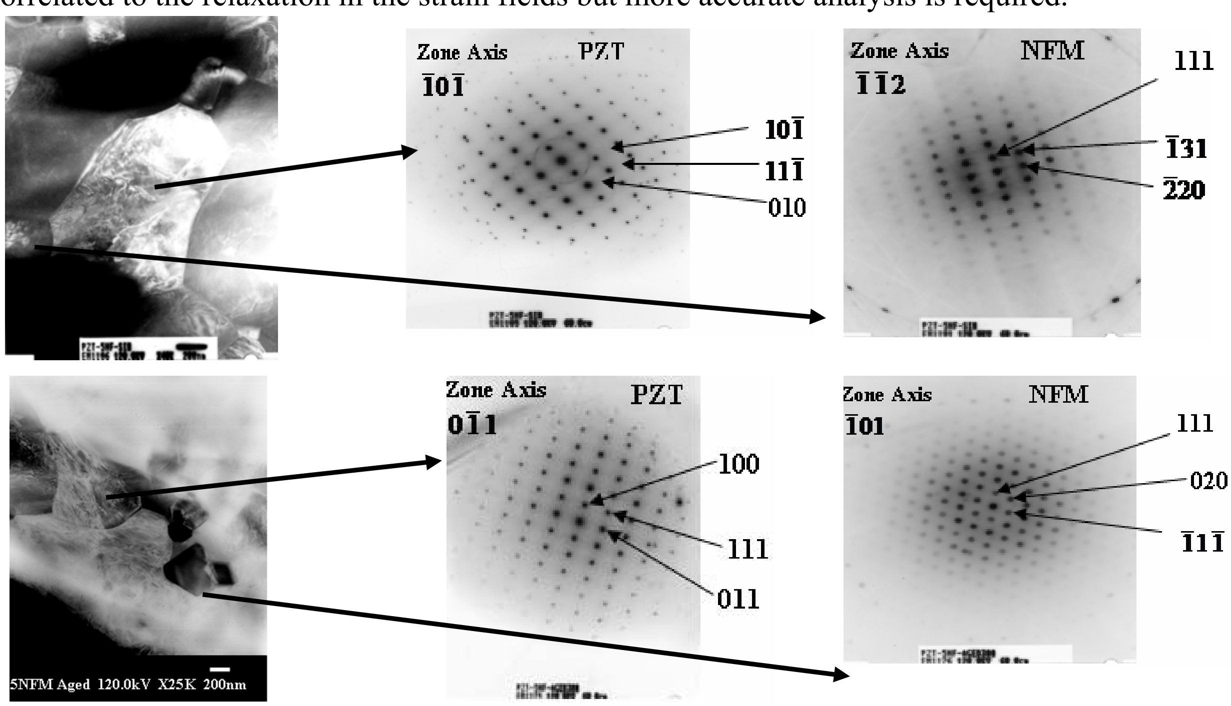

Figure 2: Spot diffraction pattern of the PZT– NFM samples (a) sintered and (b) aged condition.

Figure 3 shows the bulk ME response of the composites in the sintered, annealed, and aged states. A change of the order of 50% was obtained which needs to understood in terms of the changes in the grain structure and interface structure. Samples of the composites have been shipped to VT for the analysis of the local ME response using the PFM and MFM. Further, VT is also going to conduct magnetostrictive measurements on the samples to determine the exact changes in permeability. Meanwhile, we are performing more analysis using the XRD and TEM to conclusively tie the role of interfacial changes with the ME response.

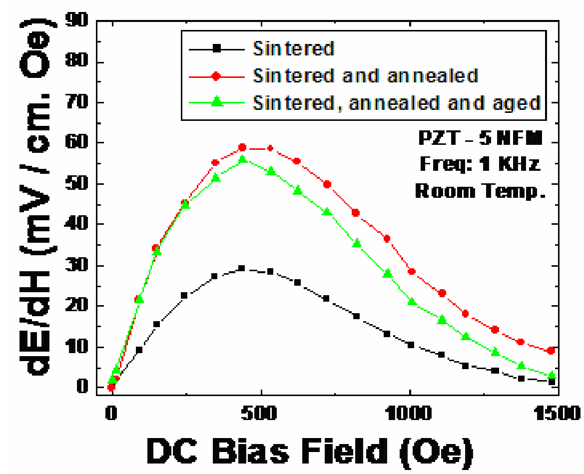

Figure 3: ME response of the PZT – NFM samples in the sintered and aged conditions.

We have just started to extend our analysis to (1-x)BTO – xCFO system. We synthesized the composites near the eutectic composition for x = 0.30 and 0.35 and a cofired bilayer composite for x = 0.335. The two very unique interfaces will be characterized to understand how they differ in their contribution towards the ME response. Preliminary results from this study are very exciting. Figure 4 shows the SEM microstructure of the two types of interfaces.

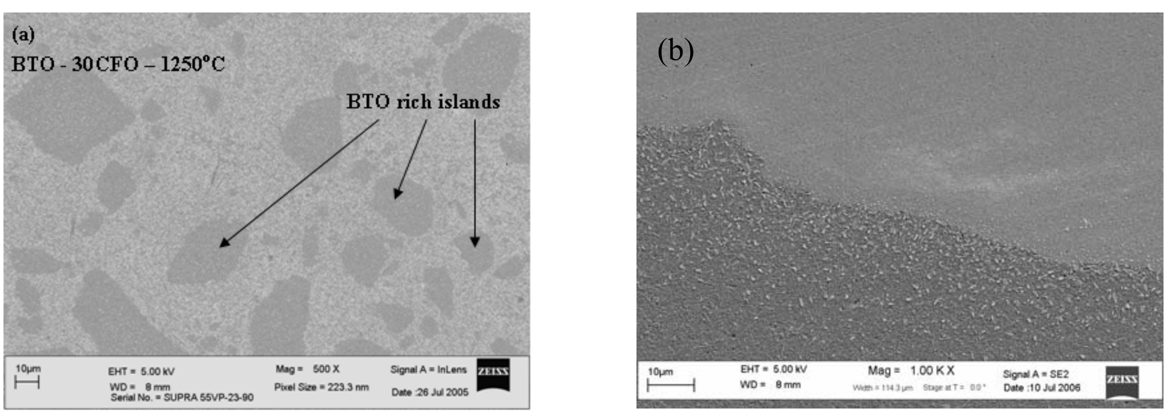

Figure 4: Microstructures of the synthesized BTO-CFO composites (a) eutectic decmposition, and (b) bilayer composite.

For the eutectic decomposition, high resolution scanning electron microscopy images revealed BTO - rich regions dispersed in a BTO-CFO matrix, where with increasing CFO content the number and size of the BTO rich regions decreases. X-ray mapping confirmed that the matrix was rich in Co and Fe. The interface thickness between the BTO rich regions and the matrix was extremely small (measurement in progress using SEM/FIB) indicating excellent matching between the two phases as shown in Fig. 5. A clear boundary between a strained BTO–CFO (i.e., matrix) and BTO-rich (i.e., multi-grain islands) phases is distinguishable, as indicated by elllipse. The deformation of the matrix was found to be due to the formation of twin-bands, which reduces the excess strain imposed by the inclusions. Magnified (10^5x) images of the microstructure taken from (b) a BTO-rich island, and (c) the CFO-rich matrix showed that the grain sizes of both regions are quite small: the average grain size in the BTO-rich islands was ~150nm and that of the CFO-rich matrix region was ~215nm. X-ray mapping about the interfacial region revealed that the distribution of Co and Fe was more concentrated in the matrix. Standard-less quantitative analysis determined the concentrations of Co and Fe to be (i) 10at% and 7at% respectively, in the BTO-rich regions; and (ii) 18% and 35% respectively, in the matrix. We have just started the TEM analysis of the BTO – CFO composites which will provide us the useful information required to understand the crystallography of the interface. Further, measurements are also being initiated on the electrical and magnetic response as a function of temperature. In near future, we will start to conduct the comparative analysis of the microstructures shown in Fig. 4(a) and (b) which will allows us to delineate the role of the elastic-coupling and magnetic flux gradient towards the local ME response. Dr. Viehland will be conducting the measurement of the local ME response using the modified MFM technique established in his laboratory.

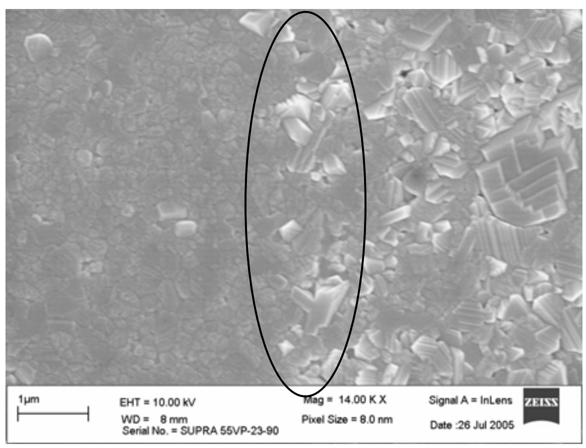

Figure 5: Interface structure in the BTO – CFO near eutectic composition.

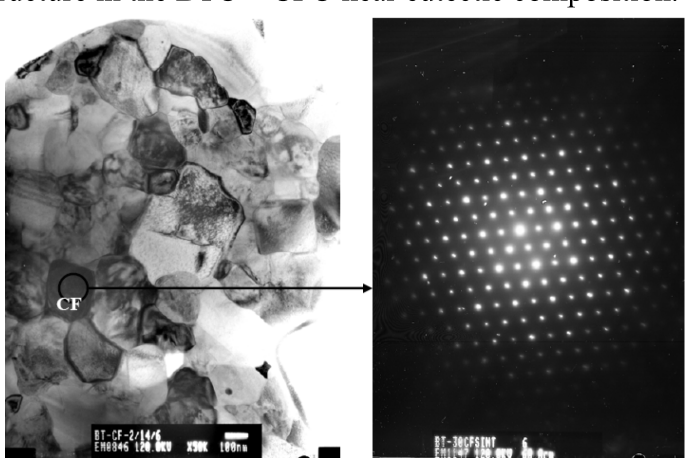

Figure 6: TEM micrograph and spot diffraction pattern of the BTO – CFO composites.

5. A list of papers (already published, in press, submitted) in which DOE support is acknowledged.

S. Priya, R. Islam, S. Dong, and D. Viehland, "Advancement in the studies on magnetoelectric composites", J. Electroceram., (2007) (in press).

R. A. Islam and S. Priya, "Magnetoelectric properties of the lead–free cofired $BaTiO_3$–$(Ni_{0.8}Zn_{0.2})Fe_2O_4$ bilayer composite", Appl. Phys. Lett. **89**, 152911 (2006).

This year Dr. Priya and Dr. Viehland are co-organizing a symposium in MS&T'07 conference on the subject of Ferroelectrics and Multiferroics. We will continue to organize this symposium at MS&T conference each year along with Dr. Khachaturyan.

6. A list of people working on the project –graduate students, postdocs, visitors, technicians, etc. Indicate for each whether receiving full or partial support. In case of partial support indicate percentage of support.

Rahul Mahajan (Ph.D. student) – 100% support. He started his Ph.D. in August 2006.

Shashank Priya (PI)

7. Planned activities for next year, which could be a short paragraph.

Our efforts will on synthesizing the high quality nanocomposites in the BTO-CFO (with and without Sr substitution) and BTO – MZF systems using controlled precipitation technique. The synthesized nanocomposites will be used to conduct structural and domain analysis using XRD, TEM, and PFM (at VT). Local electrical and magnetic response of the samples will be measured using PFM and MFM. We will also initiate measurement of the properties as a function of temperature and magnetic field.
A compilation of all the results obtained in the study will be provided to Rutgers University in next few months where the parameters will be used for the phase field modeling.

8. An update list of other support (current and pending, federal and non-federal.) For each, indicate the overlap, if any, and/or distinctiveness with the DOE-supported project. This could be brief – one or two sentences.

- Proposal Title: *Wind Powered Wireless Sensor Networks*
  Source of Support: Texas Education Coordinating Board
  Award Amount: 100,000
  Period Covered: 05/01/06 – 04/31/07
  Percent Effort: 0

- Proposal Title: *Embedded Microsensor and Microactuator Arrays for Harsh Environments (Co-PI, PI: Dan Popa)*
  Source of Support: Office of Naval Research
  Award Amount: 800,000
  Period Covered: 10/01/06 – 09/30/07
  Percent Effort: 1 summer

- Proposal Title: *Piezoelectric Fiber Composite Energy Harvesting*
  Source of Support: Advanced Cerametrics Inc.
  Award Amount: 59,075
  Period Covered: 3/01/07 – 10/30/07
  Percent Effort: 0

9. Cost status: Show approved budget by the budget period, actual costs incurred by the date of the report and projected unspent funds at the end of the current budget period. If any cost-sharing is required, breakout by DOE share, recipient share and total costs.

Total approved budget for the period – $50,468. All the money will be used by the end of the period.

To date excluding the summer salaries, there is $907 remaining as travel money, and approximately $2200 in the materials and supplies (some bills are pending). This money will be used to conduct research for next three months.