THEORY AND PRODUCTION OF LAMINATE COMPOSITES

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Predicting Magnetoelectric Voltage Coefficients of Magnetostrictive/Piezoelectric Laminate Composites:

Replicating the Research of Dong, Li, and Viehland

Introduction

Previous analysis and research on magnetostrictive-piezoelectric laminate composites have focused on layers that were poled and magnetized along their thickness directions. These designs have shown relatively large magnetoelectric coefficients under large direct current magnetic bias. Different methods have been used to determine the ME coefficient for these laminates. These methods include the Composite Averaging Method, Simple Static Elastic Method and Green's Functional Approach, and Eigenstrain Formulation. The problem with these methods is that they do not account for dynamic drive which is the operational condition under which energy is transduced in a laminate composite.

In an effort to find a better method to model the ME behavior of laminate composites, Dong, Li and Viehland used an equivalent circuit approach. This approach is based on the piezoelectric and magnetostrictive constitutive equations and an equation of motion (via strain-stress coupling between layers). Dong, Li, and Viehland used this approach to predict the ME voltage coefficients of laminates that were either poled and/or magnetized in either the longitudinal and/or transverse directions. The explicit formulas that they derived using an equation of motion and an equivalent circuit approach has proven to be equivalent to tested samples.

Design of the Laminates:

In their research, Dong, Li and Viehland constructed a 3-layer laminate (a PZT plate surrounded by 2 Terfenol-D plates). These laminates had dimensions of 12 mm by 6 mm by 2.5 mm. While the dimensions for the laminates remained constant, the thickness ratio, *n*, of the Terfenol-D layers to the thickness of the entire composite varied. Furthermore, Dong, Li and Viehland also researched how different directions for magnetization and polarization impacted the ME voltage coefficients. As seen in the diagram to the right, when a laminate was both magnetized and polarized parallel to its chief vibration direction, it was labeled as an L-L (longitudinal-longitudinal) laminate. Likewise, when a laminate was magnetized perpendicular to and polarized parallel to its chief vibration direction, it was labeled as a T-L (transverse-longitudinal) laminate.

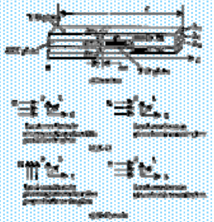


Diagram 1 (Dong, S. 2003, *IEEE Trans*)

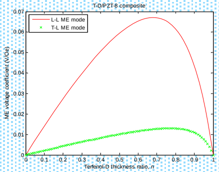
Equations to Predict the ME Voltage Coefficient under Low Frequency:

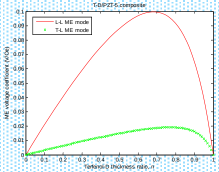
$$\left|\frac{dV}{dH_3}\right|_{L-L} = \beta \frac{n(1-n)Ad_{33,m}d_{33,p}g_{33,p}}{s_{33}^E\left[ns_{33}^E(1-k_{33}^2)+(1-n)s_{33}^H\right]}$$

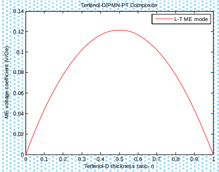
$$\left|\frac{dV}{dH_3}\right|_{T-L} = \beta \frac{n(1-n)Ad_{31,m}d_{33,p}g_{33,p}}{s_{33}^E\left[ns_{33}^E(1-k_{33}^2)+(1-n)s_{11}^H\right]}$$

$$\left|\frac{dV}{dH_3}\right|_{L-T} = \beta \frac{n(1-n)Ad_{33,m}d_{31,p}^2}{\varepsilon_{33}^T s_{11}^E\left[ns_{11}^E(1-k_{31,p}^2)+(1-n)s_{33}^H\right]}$$

These equations illustrate a few different valuable concepts. First, that there are a number of factors that influence the ME voltage coefficients of these laminates (not just the piezoelectric constants). Also, that there is a linear relationship between V and H_{ac}. Lastly, that there exists a maximum value for *n* (as illustrated in the graphs below).







Implications of Research:

This research is important to this lab's work for two reasons. First, laminate designs of this type and size are used in the field of magnetic sensors. Second, it is possible that the methods Dong, Li, and Viehland used to derive the predictive equations for these laminates could be used to derive similar equations for nano-type films.

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2.) S. Dong, J.-F. Li, and D. Viehland, "Longitudinal and transverse magnetoelectric voltage coefficients of magnetostrictive/piezoelectric laminate composite: Experiments," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 51, no. 7, pp. 794-799, 2004.

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Thin-Film Ferrites Using Spin-Spray

Spin-Spray: A new method for thin-film production

There are many methods currently used to deposit a nanoscale film on substrates in order to enhance or modify their electrical properties. The spin-spray process accomplishes this goal by applying a mist of precursor solutions containing metal ions which can be bonded to the surface of the substrate using an oxidizing agent and a buffer to maintain a basic pH. (Diagram A and Photo) The reaction is confined to the surface by excluding oxygen from the reaction area. This process builds layer by layer, passing the substrate repeatedly through the mist of precursors followed by the oxidizer.(Diagram B)

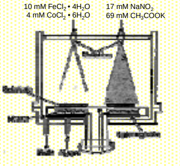

Diagram A (after Abe M.2000. Electrochim Act.)
Photo of spin-spray to right

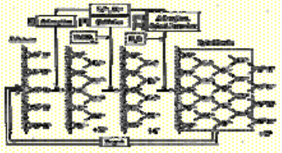

Diagram B (Abe, M. 2000 MSR Bulletin)

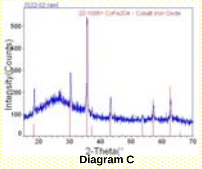

Diagram C

For this process, metal ions must be deposited at a lower oxidation state than the ions required for the final film. Also, the ions must be made available at close to room temperature without adding impurities such as organic ligands.

The CM^{3}IC group successfully produced $CoFe_2O_4$ using spin-spray. Results were confirmed by X-ray Diffraction (XRD, Diagram C) to demonstrate that experimental composition matches the expected XRD peaks.

Current Challenge: the Incorporation of Titanium into Spin-Spray Films

The spin-spray system offers broader applications to thin-film technology by allowing the development of thin films on new materials that can not withstand the conditions required for depositing thin-films by other technologies such as laser-assisted thin film deposition, electroplating, or plasma vapor deposition. Incorporating new metal ions such as titanium into the ferrite films has remained a challenge; there is no literature demonstrating successful incorporation to date. Titanium (III) and titanium (IV) ions reach an equilibrium that strongly favors the later species. The strongly acidic conditions created in shifting the equilibrium toward Ti^{3+} will strip the substrate of the hydroxide ions that assist in the building of the thin-film. Furthermore, the titanium (IV) chloride produced in this reaction is unstable in solution.

$$2\ TiCl_{3(aq)} + 2\ HCl_{(aq)} \rightleftharpoons 2\ TiCl_{4(aq)} + H_{2(aq)}$$

$$TiCl_{4(aq)} + 2\ H_2O_{(l)} \rightarrow TiO_{2(s)} + 4HCl_{(aq)}$$

Prospects for Titanium-ferrite using Spin Spray

Han (1991) and Li (2006) noted that the titanium (III) ion can be stabilized using urea as an organic ligand. The complex formed by reacting $TiCl_3$ with urea is $\mathbf{Ti((NH_2)_2CO)_6Cl_3}$, a water-soluble purple crystal. Once applied to the substrate, however, applied heat should break the urea ligand, making the Ti^{3+} available for oxidation as part of the thin film. This has already been tested on the solid Ti-urea complex One advantage of the TI-urea complex for spin-spray is that can make use of a new one-solution process for spin-spray which makes use of urea.(Subramani, 2007) In this process, the decomposition of urea produces aqueous ammonia which serves as an oxidizing agent. $(NH_2)_2CO_{(aq)} + H_2O_{(l)} \rightarrow 2\ NH_{3(aq)} + CO_{2(g)}$

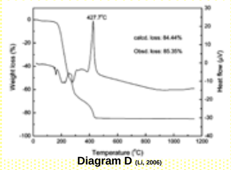

Diagram D (Li, 2006)

While this process was not envisioned for spin-spray, Li et al (2006) show that the Ti^{3+} complex will decompose, and that the urea ligand will further decompose. (Diagram D) We have already confirmed that in solution, urea will decompose at 90 °C, a useful temperature for spin-spray. However, we have not yet determined the temperature required to break the urea ligand from aqueous Ti complex. If the temperature required to break the urea ligand is over 100 °C, then the process will need to be carried out under additional pressure to prevent the boiling of the water solvent. Once these steps are determined, trials will be needed to determine ideal millimolar ratios for precursors, oxidizer, and buffer for spin-spray. The ratio will be adjusted based on XRD analysis of films produced. In cobalt-ferrite films, for example, the ratio of Fe:Co used was greater than the stoichiometric ratio suggested by the films composition.

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Classroom Connections

Teaching Linear Regression to Pre-Algebra and Algebra Students

Much of the analysis done in a lab setting involves attempting to find a relationship between collected data. At times, there may be a linear, quadratic, or exponential relationship between the different variables. Furthermore, scientists often need to determine how and why experimental results may differ from theoretical results. These concepts can be introduced to middle school students during a unit on linear regression. During one lesson the students will engage in throughout the course of this unit, they will compare the actual weight of backpacks to their estimated weight. This lesson will serve as an introductory lesson to linear regression and an analysis of how and why experimental results may differ from theoretical results. As a final project for this unit, students will investigate possible correlations between a person's hand length and their other characteristics. This project will illustrate how the knowledge of one variable can provide insight into the value for another variable. This unit will emphasize data collection, organization, representation (using appropriate software), and analysis.

Integrating Oxidation-Reduction Chemistry

Few topics covered in an initial chemistry survey course present as many challenges as the study of oxidation-reduction (redox) reactions. The movement of electrons is one of the most abstract concepts students will encounter. While the spin-spray process seems remote from high school chemistry, it is based on the redox chemistry that we expect our students to understand and apply: it is the chemistry of pushing electrons to manipulate matter. In the laboratory, however, redox is not a confined unit but a basic underlying principle that is routinely applied to create the products desired. To replicate these experiences, I plan to incorporate redox chemistry throughout the school year so that the "unit" on redox is not segregated in student's understanding but part of a natural progression. This will be accomplished through the modification of current labs and the creation of new challenges. There are two new key challenges: constructing an activity series and using that to organize a series of color changing redox reactions; and constructing a voltaic cell in order to run a useful tool of their design. These activities will allow students to better understand the work of chemists in predicting and applying the movement of electrons as a way of manipulating matter.

Research Experiences for Teachers at Northeastern University
Claire Duggan, Program Director

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