Magnetoelectric effects in piezoelectric/soft magnetic amorphous FeCo-based ribbon composites

Do Thi Huong Giang1, Le Khac Quynh2, Nguyen Van Dung3 and Nguyen Hoang Nghi3

1 Laboratory for Nano Magnetic Materials and Devices, Faculty of Engineering, Physics and Nanotechnology, 144 Xuan Thuy Road, Cau Giay, Hanoi, Vietnam
2 Hanoi University of Education 2, Xuan Hoa Community, Phuc Yen District, Vinh Phuc, Vietnam
3 Laboratory of Amorphous and Nanocrystalline Materials, Hanoi University of Technology, Vietnam

E-mail: giangdth@vnu.edu.vn

Abstract. Magnetoelectric effect has been investigated in several multiferroic laminates generated by inserting a lead-zirconate titanate PZT plate between sheets of highly soft magnetic amorphous FeCo-based alloy ribbon. The results show that the magnetoelectric coefficient $\alpha_E$ ($= dE/dH$) depends on the rest glass-forming elements as well as the concentration of Co substitution. Giant magnetoelectric is found for the composite of Fe$_{73.5}$Cu$_1$Nb$_3$B$_9$Si$_{13.5}$ ribbon, where $\alpha_E$ as high as 1000 mV/cmOe at low field of 50 Oe. $\alpha_E$ can be further improved up to 1170 mV/cmOe at 20% Fe substituted by Co. The higher the Co concentration, the lower magnetoelectric effect is observed. High magnetoelectricity at low field makes these composites suitable for special applications such as smart sensors for detecting microtesla magnetic fields and especially biosensor for magnetic label detection.

Keywords: Magnetoelectric, magnetostrictive, soft magnetic ribbons, piezoelectric.

1. Introduction
Over the past several decades, melt-spun Co- and Fe-based alloys have been extensively investigated for applications in magnetic devices requiring magnetically soft materials [1]. Because there is no crystalline magnetic anisotropy, these alloys exhibit very good soft magnetic properties in the amorphous state by a high saturation magnetization for Fe-based alloys and high permeability for Co-based alloys [2]. Up to date, most researches have mainly focused on improving their magnetic properties and exploiting their application ability in components of devices [3]. Amorphous magnetic ribbons containing about 70-85 at % of the transition metals Fe and Co and the rest glass-forming elements (e.g. B, Si, Nb, Cu, Cr, etc…) are well known as materials with excellent soft magnetic properties. Although these alloys possess an extremely low magnetostriction ($\lambda_s \sim 10^{-6}$) compared with the conventional rare earth - transition metal intermetallic compound ($\lambda_s \sim 10^{-3}$), their superior soft magnetostrictive properties at low-field is rather promising for magnetostriction-based applications. However, this advantage has not been taken into consideration.

Regarding the magnetostriction-based applications, multiferroic composites using magnetostrictive ferrites have been studied intensively from the beginning of this century [4 and refs. therein]. In these
materials, an electric polarization can respond to an applied magnetic field. In applied \textit{dc} magnetic fields ($H$), the sample undergoes poling that creates an electric field $E = \alpha_E H$, where $\alpha_E$ denotes the magnetoelectric (ME) voltage coefficient. As a result, a ME-voltage $V_{ME} = t E = \alpha_E t H$ appears between the surface of the sample with thickness $t$. Large magnetoelectric voltage coefficients $\alpha_E = dE/dH = V_{ME}/h_{ac}$ offer potential device applications as highly sensitive magnetic field sensors, microwave filters, transformers, gyrators, \textit{etc.} \cite{4}. It has been already reported that to obtain a large ME voltage at low magnetic fields in these composites, the magnetostrictive phase must have a large magnetostriction ($\lambda$) and large magnetostrictive susceptibility ($d\lambda/dH$) \cite{5}. In the light of these requirements, the amorphous FeCo-based ribbons are extremely suitable for use in ME composites. Besides their magnetic and magnetostrictive softness advantages, it must be mentioned the cheap materials constituted, low cost and simple preparation techniques. In the frame of this paper, we focused to study the magnetoelectric effect in the piezoelectric/soft magnetic amorphous FeCo-based alloy ribbon composites and their application ability in biosensor for magnetic label detection. The dependence of ME effect on the rest glass-forming elements as well as concentration of the Co substitution will be considered and studied.

2. Experimental
Amorphous FeCo-based ribbons with different glass-forming elements (\textit{e.g.} B, Si, Nb, Cu, Cr, \textit{etc.}…) and Co concentration have been prepared by the melt-spinning technique. The ME composites are formed by bonding an out-of-plane poled piezoelectric PZT plate (APCC-855) with thickness $t_{PZT} = 200 \mu$m (supplied by the American Piezoceramics Inc) between ribbon sheets in size 5x5 mm. The optimum configuration for this ME composite uses two ribbon sheets bonded on both sides of PZT plate (figure 1) \cite{6}. Thanks to mechanical coupling between these components, when the magnetostrictive sheets are strained under applied in-plane magnetic fields, the PZT plate will undergo a forced strain. In this case, the ME-voltage $V_{ME}$ is induced across the thickness of the piezoelectric plate. Practically, the $V_{ME}$ is measured directly as a response of the ME composite to a weak \textit{ac} magnetic field $h = h_0 \sin(2\pi f_0 t)$ oscillating at resonant frequency of 2.5 kHz in a \textit{dc} bias field $H$ provided by an electromagnet. A lock-in amplifier (7265 DSP) is used to generate a controllable input current to the \textit{ac} field coil and to measure the output voltage ($V_{ME}$) induced across the PZT layer. The magnetization was recorded by a Lake Shore 7400 series VSM.

3. Results and discussion
3.1. Dependence of ME effect on glass-forming elements
Shown in figure 2 are hysteresis loops and ME coefficient respects to \textit{dc} magnetic field of three composites of three typical ribbons with composition Fe$_{76.5-x}$Cr$_x$B$_{10}$Si$_{13.5}$ with $x = 0$, 2 and 4 at\%. As seen clearly in this figure that all these ribbons exhibit extremely low magnetic coercivity (less than 0.5 Oe) but very different magnetically softness depending on the Cr concentration. The more Cr concentration, the higher slope angle of the loop will be achieved. The optimum magnetic softness with highest slope is observed in the ribbon with 4 at\% Cr. Consequently, the high magnetoelectric softness characterized by the low magnetic field $H_o$, where the ME coefficient is expected to be optimum at 4\% Cr. Indeed, $H_o$ is decreased from 205 Oe to 100 Oe with increasing $x$ from 0 to 4 at\%. Although having better low-field ME effect, the ribbon with higher Cr ($x = 4$) give lower maximum value $\alpha_E$ of 680 mV/cmOe rather than that of 800 mV/cmOe in the case without Cr ($x = 0$). That can be well understood by the higher rest glass-forming elements concentration lowers the saturation magnetostriction due to their non magnetostriction contribution, thereby, lower maximum ME coefficient. For sensor application to detect \textit{dc} magnetic field, the sensitivity of output voltage $S_{H}$ with respects to magnetic field is most important. $S_{H}$ reaches maximum of 0.75 mV/Oe in the ribbon with 4 at\% Cr.
Figure 1. Schematic illustrations of ME composite based on amorphous magnetic FeCo-based ribbons (with double ribbon sheets on each outer side).

Figure 2. Relative magnetization (a) and ME coefficient (b) vs magnetic dc field for composites of Fe-based ribbons with different glass-forming Cr concentration ($x$).

Figure 3. ME coefficient (a) and ME voltage (b) as a function of dc and ac magnetic fields, respectively, for the composites of Fe-based ribbons with and without small amounts of glass-forming Cu and Nb.

The ME effect can be significantly improved in the ribbon with small amounts of Fe substituted by Cu and Nb. In this case, the optimum composition has found in the composite of Fe$_{73.5}$Cu$_1$Nb$_3$B$_8$Si$_{13.5}$ (Finemet) ribbon, where $\alpha_E$ as high as 1000 mV/cmOe obtained at very low magnetic fields of 50 Oe (see in figure 3a). In addition, the slope of ME coefficient respect to the external field close to zero is much higher compared with that without Cu and Nb giving a sensitivity $S_{H}$ of 2.8 mV/Oe, four times
higher than that without Cu and Nb. It shows application ability to use this composite in sensor highly sensible to low magnetic field. This magnetoelectric sensor can sense not only dc magnetic field but also especially with minus ac magnetic field. Shown in figure 3b is the variation of ME-voltage as a function of ac field measured at resonant frequency. The composite using Fe_{73.5}Cu_{1}Nb_{3}B_{9}Si_{13.5} ribbon reveals a higher sensitivity, whereas the linear range respects to ac field is larger in the composite of Fe_{76.5}B_{10}Si_{13.5} ribbons.

3.2. Dependence of ME effect on Co addition
Various composites using Fe_{100-y}Co_{y}-based ribbons with different composition of Co (y) have been prepared and investigated. The hysteresis loops and ME coefficient are shown in figure 5. The higher Fe concentration substituted by Co exhibits better magnetic softness with higher low-field slope and lower saturation field (figure 5a). As a consequent, the magnetic field $H_o$ at which the $\alpha_E$ reaches maximum is decreased from 200 to 60 Oe with the increase of y from 0 to 100 %. Whereas, the highest value of $\alpha_E$ of about 1170 mV/cmOe at 120 Oe was observed in the ribbon with 20 at% Fe substituted by Co. High Co concentration leads to lower $\alpha_E$ and almost vanished ($\alpha_E = 6$ mV/cmOe) at concentration more than 90%. These findings can be attributed to the strong relationship between ME voltage and the magnetostrictive susceptibility ($d\lambda/dH$) of the magnetic ribbon, $V_{ME} \sim d\lambda/dH$ [7]. As we known that the magnetic elements Fe and Co in their pure crystalline forms have positive and negative magnetostriction, respectively. The amorphous Fe-based alloys have high positive magnetostriction $\lambda$ of about $30 \times 10^{-6}$ [8] compared with negative or nearly zero magnetostriction ranging between $-6 \times 10^{-6}$ and $-0.1 \times 10^{-6}$ [9] of Co-based alloys. As a result, the ME effect is null at more than 90% Fe substituted by Co due to zero magnetostriction caused by Co atom cancelled out part of the positive magnetostriction. The optimum concentration for ME effect is observed at 20 at% Co because of both their high $\lambda$ and $d\lambda/dH$ [6]. Further decreasing Co concentration will lower the ME effect due to the decline of $d\lambda/dH$.

![Figure 4](image)

**Figure 4.** Relative magnetization (a) and ME coefficient (b) vs magnetic dc field for composites based on amorphous magnetic Fe_{100-y}Co_{y}-based ribbons with different Fe concentration (y) substituted by Co.

For magnetoelectric sensor applications, the Fe_{80}Co_{20}-based ribbon will be the best candidate. That gives both high magnetoelectric effect and sensitivity ME-voltage at low magnetic field [6]. This sensor is promising not only for microtesla magnetic field sensors but also for biosensor applications. Here, for biosensor fields to detect magnetic labels, we also start studying the potentiality of using this composite for magnetic nanoparticles detection. Shown in figure 5 is real-time voltage change for the detection of nickel ferrite (NiFe_{2}O_{4}) nanoparticles using composite of Fe_{60}Co_{20}-based ribbon. There are two cycles where the high state shows the signals after dropping 2µl of the NiFe_{2}O_{4} solution (5 wt%) on the surface of the composite and the low state shows the signals after washing (figure 5,
As seen from this figure, the total output signal changes were found of about 30 μV. After further process with another droplet/washing cycle, the similar signal response was repeated. This voltage response can be much higher by increasing the ac magnetic field.

This high value of nanoparticles response may recommend our future work in developing biochip for biosensor based on our composites. For a real biosensor application to detect magnetic labels, this sensor is required to diminish in micrometer-size. The project is still in progress.

Figure 5. Real-time voltage changes for nickel ferrite nanoparticles detection using composite of Fe₈₀Co₂₀-based ribbon. This profile was carried out in an applied magnetic field of 5 mT.

4. Conclusion remarks

Although amorphous FeCo-based ribbons possess an extremely low magnetostriction (λₐ = 10⁻⁶), their superior soft magnetic and magnetostrictive properties is promising for low-field magnetoelectric applications. The magnetoelectric investigations in the composites generated by inserting a PZT plate between melt-spinning ribbon sheets show that the magnetoelectric effect depends on the concentration of the Co substitution as well as the rest glass-forming elements. The giant magnetoelectric αₑ as high as 1000 mV/cmOe at very low field of 50 Oe is found for the composite of Fe₇₃.₅Cu₁.₅Nb₃.₅B₉Si₁₃.₅ ribbon. This coefficient can be further increased up to 1170 mV/cmOe by substituting 20% Fe by Co. The highly magnetoelectricity at low field makes these composites promising for applications in magnetic sensor and biosensor fields.

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