Structural Effects of Magnetostrictive Materials on the Magnetoelectric Response of Particulate CZFO/NKNLS Composites

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Abstract: In this study, magnetostrictive powders of CoFe$_2$O$_4$ (CFO) and Zn-substituted CoFe$_2$O$_4$ (CZFO, Zn = 0.1, 0.2) were synthesized in order to decrease the optimal dc magnetic field ($H_{\text{opt.}}$), which is required to obtain a reliable magnetoelectric (ME) voltage in a 3-0 type particulate composite system. The CFO powders were prepared as a reference via a typical solid solution process. In particular, two types of heterogeneous CZFO powders were prepared via a stepwise solid solution process. Porous-CFO and dense-CFO powders were synthesized by calcination in a box furnace without and with pelletizing, respectively. Then, heterogeneous structures of pCZFO and dCZFO powders were prepared by Zn-substitution on calcined powders of porous-CFO and dense-CFO, respectively. Compared to the CFO powders, the heterogeneous pCZFO and dCZFO powders exhibited maximal magnetic susceptibilities ($\chi_{\text{max}}$) at lower $H_{\text{dc}}$ values below ±50 Oe and ±10 Oe, respectively. The Zn substitution effect on the $H_{\text{dc}}$ shift was more dominant in dCZFO than in pCZFO. This might be because the Zn ion could not diffuse into the dense-CFO powder, resulting in a more heterogeneous structure inducing an effective exchange-spring effect. As a result, ME composites consisting of 0.948Na$_{0.5}$K$_{0.5}$NbO$_3$–0.052LiSbO$_3$ (NKNLS) with CFO, pCZFO, and dCZFO were found to exhibit $H_{\text{opt.}} = 966$ Oe (NKNLS-CFO), $H_{\text{opt.}} = 689–828$ Oe (NKNLS-pCZFO), and $H_{\text{opt.}} = 458–481$ Oe (NKNLS-dCZFO), respectively. The low values of $H_{\text{opt.}}$ below 500 Oe indicate that the structure of magnetostrictive materials should be considered in order to obtain a minimal $H_{\text{opt.}}$ for high feasibility of ME composites.

Keywords: structural effect; magnetostrictive powders; hysteretic magnetization; magnetoelectric voltage; optimal dc magnetic field; particulate composites; CZFO; NKNLS

1. Introduction

Since the year 2000, magnetoelectric (ME) response has been a topic of interest in the development of energy-harvesters, sensitive magnetic sensors, and magnetically driven memories, or magnetoelectric transducers [1–3]. The ME effect is a result of induced piezoelectric effect (electrical effect/mechanical) in a piezoelectric phase by strain transfer of the magnetostrictive effect (mechanical/magnetic) in a magnetostrictive phase [4–8].

$$\text{ME effect} = \frac{\text{electric}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}}$$ (1)

However, reliable ME voltage from 3-0 type particulate composites can only be obtained under an optimal dc magnetic field ($H_{\text{opt.}}$) on the order of over several thousand Oersteds (Oe), which is a serious drawback limiting practical ME applications [9,10]. According to previous studies on particulate...
ME composites, a maximum ME voltage ($\Delta ME$) was obtained at high values of $H_{\text{opt}}$ above 1000 Oe from various compositions of Pb(Zr$_{0.52}$Ti$_{0.48}$)$_{3-x}$Ni$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ ($\Delta ME = 54.4$ mV/cm-Oe at $H_{\text{opt}} = 1000$ Oe), BaTiO$_3$-Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ($\Delta ME = 73$ mV/cm-Oe at $H_{\text{opt}} > 2000$ Oe), BaTiO$_3$-CoFe$_2$O$_4$ ($\Delta ME = 17.04$ mV/cm-Oe at $H_{\text{opt}} > 15,000$ Oe), Ba$_{0.85}$Ca$_{0.15}$Ti$_{0.9}$Zr$_{0.1}$O$_3$-CoFe$_2$O$_4$ ($\Delta ME = 1.028$ mV/cm-Oe at $H_{\text{opt}} > 8000$ Oe), and Na$_{0.5}$Bi$_{0.5}$TiO$_3$-CoFe$_2$O$_4$ ($\Delta ME = 0.42$ mV/cm-Oe at $H_{\text{opt}} > 2500$ Oe) [11–15]. Even though lower $H_{\text{opt}}$ values of 500–1000 Oe were reported when investigating the size effect of magnetostrictive particles in BaTiO$_3$-NiFe$_{1.98}$O$_4$ ($\Delta ME = -252$ mV/cm-Oe at $H_{\text{opt}} = 500–1000$ Oe), the sintering temperature effect in Pb(Zr$_{0.52}$Ti$_{0.48}$)$_3$-NiCo$_{0.02}$Cu$_{0.02}$Mn$_{0.1}$Fe$_{1.8}$O$_4$ ($\Delta ME = 63$ mV/cm-Oe at $H_{\text{opt}} = 600$ Oe), and the piezoelectric phase effect in Pb(Zr$_{0.52}$Ti$_{0.48}$)$_3$-Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($\Delta ME = 190$ mV/cm-Oe at $H_{\text{opt}} = 800$ Oe), there is still a need to decrease $H_{\text{opt}}$ below 100 Oe for a high feasibility of particulate ME composite [16–18].

In this study, the structural effects of magnetostrictive materials on ME response was investigated in order to decrease $H_{\text{opt}}$ values in a particulate ME composite system. In particular, magnetostrictive powders of CoFe$_2$O$_4$ (CFO), Zn-substituted porous-CFO (pCZFO) and Zn-substituted dense-CFO (dCZFO) were respectively prepared to explore structure-dependent hysteretic magnetizations. Then the $H_{\text{opt}}$ shift in ME response was analyzed in particulate ME composites consisting of each magnetostrictive powder (CFO, pCZFO, and dCZFO) in a 0.948Na$_{0.5}$K$_{0.5}$NbO$_3$–0.052LiSbO$_3$ (NKNLS) piezoelectric matrix.

2. Experimental

Figure 1a-c shows a schematic diagram of the experimental procedure based on a solid-solution method to synthesize magnetostrictive powders of CFO, pCZFO, and dCZFO, respectively. As shown in Figure 1a, for preparation of CFO powders, Co$_3$O$_4$ (Sigma-Aldrich, Seoul, Korea, ≥99.5%) and Fe$_2$O$_3$ (Sigma-Aldrich, Seoul, Korea, ≥99.0%) powders were mixed by ball milling for 24 h. The well-mixed and fully dried powders were calcined at 1000 °C for 2 h. The calcined powders were ball-milled for 24 h and then sintered at 1200 °C for 2 h. After crushing and sieving of the sintered powders, CFO powders were selected with a particle size of 24–64 μm. As shown in Figure 1b,c, for preparation of pCZFO and dCZFO powders, Co$_3$O$_4$ (Sigma-Aldrich, Seoul, Korea, ≥99.5%) and Fe$_2$O$_3$ (Sigma-Aldrich, Seoul, Korea, ≥99.0%) powders were mixed by ball milling for 24 h. Then, the well-mixed and fully dried powders were calcined at 1000 °C for 2 h without and with pelletizing at 30 bar pressure, respectively. The calcined CFO powders exhibiting a porous structure (pCFO) and a dense structure (dCFO) were mixed with 0.1 and 0.2 molar ratio of ZnO powders (Sigma-Aldrich, Seoul, Korea, ≥99.0%), respectively. Then the mixed powders were sintered at 1200 °C for 2 h. After crushing and sieving of the sintered powders, pCZFO and dCZFO powders were selected with particle sizes of 24–64 μm.

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** Schematic diagram of experimental procedure based on solid-solution synthesis for (a) CoFe$_2$O$_4$ (CFO), (b) Zn-substituted porous-CoFe$_2$O$_4$ (pCZFO), and (c) Zn-substituted dense-CoFe$_2$O$_4$ (dCZFO) powders. (d) Schematic diagram of magnetoelectric measurement set up.
ME composites were prepared with a 3-0 type particulate structure consisting of the magnetostrictive powders (CFO, pCZFO, and dCZFO, respectively) in a lead-free piezoelectric matrix of NKNLS. For preparation of NKNLS powders, K$_2$CO$_3$ (Sigma-Aldrich, Seoul, Korea, 99%), Na$_2$CO$_3$ (Sigma-Aldrich, Seoul, Korea, 99.5%), Li$_2$CO$_3$ (Sigma-Aldrich, Seoul, Korea, 99%), Nb$_2$O$_5$ (Sigma-Aldrich, Seoul, Korea, 99.9%), and Sb$_2$O$_5$ (Sigma-Aldrich, Seoul, Korea, 99%) powders were mixed by ball milling for 24 h. Then, the well-mixed and fully dried powders were calcined at 880 °C for 2 h. After sintering at 1050 °C for 2 h of CFO-NKNLS, pCZFO-NKNLS, and dCZFO-NKNLS pellets with a magnetostrictive/piezoelectric weight ratio of 0.1, disk-type ME composites were prepared with a thickness of 1 mm and a diameter of 13 mm. The ME composites were poled in silicone oil at room temperature by applying a dc field of 3 kV/mm for 30 min.

Crystal structures were investigated by X-ray diffraction (XRD; Miniflex600, RIGAKU, Tokyo, Japan) with CuK$_\alpha$ (λ = 1.5406 Å) radiation. The surface morphology was investigated by scanning electron microscopy (SEM; JEOL-6700F, Tokyo, Japan). Hysteretic magnetization curves were characterized by vibrating sample magnetometry (VSM; Model 7404, Lakeshore, CA, USA). Piezoelectric constants were measured by an APC YE 2730A d33 meter (APC Inc., Mackeyville, PA, USA). ME voltages were measured by applying an $H_{dc}$ of 1 Oe at an off-resonance frequency, $f_o$ of 1 kHz using a lock-in amplifier (SR860, Stanford Research Systems Inc., Sunnyvale, CA, USA) [19,20]. As shown in Figure 1d, using the lock-in amplifier a calculated ac current was applied to a Helmholtz coil to induce an $H_{ac}$ of 1 Oe with an off-resonance frequency of 1 kHz. Then, an $H_{dc}$ of ±1000 Oe was applied to the ME samples using an electromagnet to obtain reliable ME voltages. Output ac voltage ($V_{ac}$) from the ME samples was measured by the lock-in amplifier.

3. Results and Discussion

Crystal structures of the magnetostrictive CFO, pCZFO (Zn = 0.1, Zn = 0.2), and dCZFO (Zn = 0.1, Zn = 0.2) powders were investigated from XRD patterns. As shown in Figure 2a, all magnetostrictive powders were found to exhibit XRD peaks of (220), (311), (222), (400), (422), (511), and (440) representing a spinel structure of AB$_2$O$_4$ (JCPDS card No. 22-1086) [21,22]. Even though no noticeable peak shift in the XRD patterns was observed over a wide 2θ range after Zn substitution of 0.1 and 0.2 molar ratio on the porous-CFO and dense-CFO powders, a major shift of the (311) peak at $2\theta = 35.5^\circ$ towards a lower angle by Zn substitution was observed in the XRD patterns at a narrow 2θ range, as shown in Figure 2b. Bragg’s Law can be used to calculate a lattice constant using the equation:

$$a^2 = \lambda^2(h^2 + k^2 + l^2)^{1/2} / 4\sin^2\theta$$

(2)

where $a$ is the lattice constant, $\lambda$ is the wavelength of CuK$_\alpha$ radiation, and $h$, $k$, and $l$ are the Miller indices. As the (311) peak shifts to a lower angle by Zn substitution, the lattice constant increases due to a decrease in the value of $\sin \theta$. With respect to the ionic radius, the pCZFO and dCZFO powders were found to exhibit an increased lattice constant compared to CFO powders because Zn$^{2+}$ (0.82 Å) has a larger ionic radius than Co$^{2+}$ (0.78 Å), which is replaced by Zn$^{2+}$ [23–25].
In terms of Zn substitution in the porous-CFO and dense-CFO powders, magnetic properties of saturation magnetization ($M_s$), remanent magnetization ($M_r$), coercive field ($H_c$), and magnetic susceptibility ($\chi = dM/dH$) were investigated, as shown in Figure 3 and Table 1. Compared to the CFO powders, the pCZFO and dCZFO powders were found to exhibit enhanced $M_s$ with decreased $H_c$, as shown in Table 1. The enhanced values of $M_s$ demonstrate that the addition of Zn$^{2+}$ ions causes a migration of Fe$^{3+}$ ions from a tetrahedral site to an octahedral site, which causes an increase of the total magnetic moment by reducing the net magnetic moment in the tetrahedral site. Furthermore, decreased values of $H_c$ illustrate that grain growth by Zn substitution causes an increase of the domain wall number, resulting in large grain size, which requires less energy for spin rotation [26,27]. As shown in Figure 3b,e, stepped demagnetization behavior is shown by pCZFO with Zn = 0.2 and dCZFO with Zn = 0.1 and 0.2, which might be caused by the exchange-spring effect derived from the interplay of two uniquely characteristic phases [28–30]. From the result, it is noted that dCZFO possesses a sufficient exchange-spring effect based on high interaction between two magnetostrictive phases even though the Zn substitution of 0.1 is low in the dense-CFO powders. As shown in Figure 3c,f, the pCZFO and dCZFO powders were found to exhibit higher $\chi_{\text{max}}$ of 0.22–0.42 emu/g·Oe at lower values of $H_{\text{dc}}$ below ±50 Oe, compared to $\chi_{\text{max}}$ of 0.05 emu/g·Oe at an $H_{\text{dc}}$ below ±200 Oe from the CFO powders. In particular, the $\chi_{\text{max}}$ values of dCZFO were obtained at very low values of $H_{\text{dc}}$ below ±10 Oe, which are induced by prominent stepped demagnetization behavior.
Materials 2019, 12, 1053

5 of 9

Figure 3. Hysteretic magnetization curves at (a,d) a wide $H_{dc}$ range of $\pm 10$ kOe and (b,e) a narrow $H_{dc}$ range of $\pm 1$ kOe, (c,f) magnetic susceptibilities ($\chi$) of CFO, pCZFO (Zn = 0.1, 0.2) and dCZFO (Zn = 0.1, 0.2) powders.

Table 1. Magnetic properties of CoFe$_2$O$_4$ (CFO), Zn-substituted porous-CoFe$_2$O$_4$ (pCZFO) and Zn-substituted dense-CoFe$_2$O$_4$ (dCZFO) powders; saturation magnetization ($M_s$), remanent magnetization ($M_r$), coercive field ($H_c$), and magnetic susceptibility ($\chi_{max}$ = d$M$/d$H$).

| Magnetostriective Powders | Zn Ratio | Saturation Magnetization | Remanant Magnetization | Coercive Field | Magnetic Susceptibility |
|---------------------------|----------|--------------------------|------------------------|----------------|------------------------|
|                           |          | $M_s$ (emu/g)            | $M_r$ (emu/g)          | $H_c$ (Oe)    | $\chi_{max}$ (emu/g·Oe) |
| CFO                       | Zn = 0   | 74.5 ± 0.75              | 16.8 ± 0.17            | 366.2 ± 3.66  | 0.05                   |
| pCZFO                     | Zn = 0.1 | 77.1 ± 0.77              | 18.5 ± 0.19            | 101.6 ± 1.02  | 0.22                   |
|                           | Zn = 0.2 | 75.9 ± 0.76              | 0.5 ± 0.01             | 2.4 ± 0.02    | 0.42                   |
| dCZFO                     | Zn = 0.1 | 86.3 ± 0.86              | 9.3 ± 0.09             | 36.2 ± 0.36   | 0.34                   |
|                           | Zn = 0.2 | 82.6 ± 0.83              | 2.3 ± 0.02             | 10.8 ± 0.11   | 0.35                   |

To investigate structure-dependent ME responses, particulate ME composites were prepared with compositions of CFO-NKNLS, pCZFO-NKNLS (Zn = 0.1, 0.2), and dCZFO-NKNLS (Zn = 0.1, 0.2). From the XRD patterns, as shown in Figure 4, perovskite (ABO$_3$) and spinel (AB$_2$O$_4$) crystal structures were confirmed as piezoelectric and magnetostriective phases, respectively. Even though sintering was conducted at 1050 °C for 2 h, all ME composites were found to exhibit stable crystal structures without any trace of secondary phase. In particular, a peak split at $2\theta = 45$–46° representing a tetragonal phase
was maintained during the high temperature sintering. Therefore, the ME composites were found to exhibit a piezoelectric charge constant ($d_{33}$) of 55–60 pC/N after sample poling.

Figure 4. XRD patterns of magnetoelectric (ME) particulate composites consisting of a piezoelectric phase of NKNLS and magnetostrictive phases of CFO, pCZFO (Zn = 0.1, 0.2) and dCZFO (Zn = 0.1, 0.2).

From the particulate composites of CFO-NKNLS, pCZFO-NKNLS (Zn = 0.1, 0.2), and dCZFO-NKNLS (Zn = 0.1, 0.2), ME voltage ($\alpha_{\text{ME}}$) and $H_{\text{opt.}}$ were investigated while applying $H_{\text{ac}} = 1$ Oe at $f = 1$ kHz by sweeping $H_{\text{dc}}$ of $\pm$1000 Oe, as shown in Figure 5 and Table 2. The CFO-NKNLS composites were found to exhibit a maximum $\alpha_{\text{ME}} = 140$ µV/cm·Oe at $H_{\text{opt.}} = 966$ Oe. Even though a decreased $H_{\text{opt.}}$ value of 689–828 Oe was obtained from pCZFO-NKNLS as shown in Figure 5a, there was not a sufficient $H_{\text{opt.}}$ shift due to its weak behavior of stepped demagnetization. On the other hand, the dCZFO-NKNLS composites were found to exhibit remarkable $H_{\text{opt.}}$ values of 458–481 Oe as shown in Figure 5b, which are lower $H_{\text{opt.}}$ values than any reported particulate ME composites so far. As a result, the structural effect of magnetostrictive powders on $H_{\text{opt.}}$ shift is clearly shown between the heterogeneous pCZFO and dCZFO powders. Although the obtained $H_{\text{opt.}}$ value of 458 Oe from dCZFO-NKNLS is higher than 100 Oe, this study can serve to minimize a required $H_{\text{opt.}}$ by complexation with previous studies for high feasibility of particulate ME composites.
Figure 5. ME voltage of particulate composites consisting of a piezoelectric phase of NKNLS and magnetostrictive phases of (a) CFO and pCZFO (Zn = 0.1, 0.2) and (b) CFO and dCZFO (Zn = 0.1, 0.2).

Table 2. Magnetolectric (ME) responses of CFO-NKNLS, pCZFO-NKNLS, and dCZFO-NKNLS composites; optimal magnetic field ($H_{\text{opt.}}$) and ME voltage ($\alpha_{\text{ME}}$).

| Magnetoelectric Composites | Zn Ratio | $H_{\text{opt.}}$ (Oe) | $\alpha_{\text{ME}}$ ($\mu$V/cm·Oe) |
|----------------------------|----------|------------------------|---------------------------------|
| CFO-NKNLS                  | Zn = 0   | 966                    | 140 ± 21.0                      |
| pCZFO-NKNLS                | Zn = 0.1 | 689                    | 130 ± 19.5                      |
|                            | Zn = 0.2 | 828                    | 179 ± 26.9                      |
| dCZFO-NKNLS                | Zn = 0.1 | 481                    | 228 ± 34.2                      |
|                            | Zn = 0.2 | 458                    | 184 ± 27.6                      |

4. Conclusions

In this study, magnetostrictive powders of CFO, pCZFO (Zn = 0.1, 0.2) and dCZFO (Zn = 0.1, 0.2) were prepared to produce low values of $H_{\text{opt.}}$, which is required to obtain a reliable ME voltage in a 3-0 type particulate composite system. Compared to the CFO powders ($\chi_{\text{max}} = 0.05$ emu/g·Oe at $H_{\text{dc}}$ below ±200 Oe), the pCZFO and dCZFO powders were found to exhibit higher $\chi_{\text{max}}$ of 0.22–0.42 emu/g·Oe at lower $H_{\text{dc}}$ values below ±50 Oe and ±10 Oe, respectively. The NKNLS-based ME composites consisting of CFO, pCZFO, dCZFO, respectively were found to exhibit $H_{\text{opt.}}$ = 966 Oe (NKNLS-CFO), $H_{\text{opt.}}$ = 689–828 Oe (NKNLS-pCZFO), and $H_{\text{opt.}}$ = 458–481 Oe (NKNLS-dCZFO). The results illustrate that a low $H_{\text{opt.}}$ value of 458 Oe was obtained from the effective stepped demagnetization behavior of dCZFO (Zn = 0.2), which was induced by a structural effect in a heterogeneous magnetostrictive phase.

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