

Frequency Dependent Magnetolectric Responses in [0.948 Na_{0.5}K_{0.5}NbO₃-0.052 LiSbO₃]-[Co_{1-x}Zn_xFe₂O₄] Particulate Composites

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Abstract: Magnetolectric (ME) properties of 3-0 type particulate composites have been investigated with respect to application features for reliable magnetic sensitivity and magnetically-induced output voltage. In order to figure out the magnetolectric characteristics in the ME composites, frequency dependent ME responses were studied from [0.948 Na_{0.5}K_{0.5}NbO₃-0.052 LiSbO₃]-[Co_{1-x}Zn_xFe₂O₄] (NKNLS)/Co_{1-x}Zn_xFe₂O₄ (CZFO, x=0, 0.1, and 0.2). As a result, the maximal α_{ME} of 23.15 mV/cm·Oe was achieved from the NKNLS-CZFO ($x_{Zn} = 0.1$) composites at resonance frequency of 315 kHz and $H_{dc} = 0$ Oe. From the frequency dependent ME responses, it is clearly described that the self-biased ME composites can be used for applications as both magnetic sensors and energy harvesters, respectively.

Keywords: Frequency dependent, Self-biased, Magnetolectric, Piezoelectric, Magnetostrictive, Particulate composites

In recent years, multiferroic composites consisting of piezoelectric and magnetostrictive phases have been studied due to their feasible properties for energy harvesters, highly-sensitive magnetic sensors, memory devices and so on [1,2]. Magnetolectric (ME) effect in the multiferroic composites is defined as an induced electrical polarization owing to a magnetostriction in response to an external magnetic bias field [2-5]. In the ME composites, effective magnetostrictive strain should be induced by applying an external DC magnetic field to obtain pragmatic ME voltage coefficient (α_{ME}). The requirement for external magnetic field for sufficient ME responses make a big obstacle in developing ME applications [6]. To address this problem, extensive research has been

carried out, focusing on self-biased magnetolectric effect under near zero DC magnetic fields [7,8]. Mandal et al. demonstrated a compositionally graded ferrites/Pb(Zr,Ti)O₃ laminate structure, which exhibited non-zero ME coefficient at $H_{dc}=0$ in 2010 [9]. Subsequently, Yang et al. reported conventional ME laminate composites with self-biased ME responses via optimization of compositional and electrical configurations [10]. Lage et al. proposed a new method for manifesting self-biased phenomena from a multicomponent magnetic system including antiferromagnetic and ferromagnetic phase. Those studies have used multiphase compositions in 2-2 type laminate structures [8,11,12]. Even though homogeneous phase magnetostrictive materials were considered for feasible ME applications, only few studies about the self-biased ME effect in 3-0 system have been reported [13]. This study provides a basic understanding of the self-biased ME responses in 3-0 type particulate composites consisting of Co_{1-x}Zn_xFe₂O₄ (CZFO, x=0.0, 0.1 and 0.2) [14,15]

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and $0.948\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3-0.052\text{LiSbO}_3$ (NKNLS). For the different compositions, frequency dependent ME responses were investigated aiming at magnetic sensors and energy harvesters.

CZFO magnetostrictive particles and KNNLS piezoelectric matrix were prepared by solid-state reaction [10]. To synthesize CZFO ($x_{\text{Zn}}=0.0, 0.1$ and 0.2), Co_3O_4 ($\geq 99.5\%$), Fe_2O_3 ($\geq 99.0\%$) and ZnO ($\geq 99.0\%$) (All from Sigma-Aldrich) powders were accurately weighed in the appropriate stoichiometric ratio and conveyed into a polypropylene bottle with zirconia balls and alcohol ($\geq 99.9\%$) medium for 24 h ball milling process. The totally mixed powders were calcined at $1,000^\circ\text{C}$ for 2 h. The calcinated CZFO powders were finely grounded and sintered at $1,200^\circ\text{C}$ for 2 h. The CZFO particles with the particle size below $25\ \mu\text{m}$ was achieved. To prepare NKNLS, K_2CO_3 ($\geq 99\%$), Na_2CO_3 ($\geq 99.5\%$), Li_2CO_3 ($\geq 99\%$), Nb_2O_5 ($\geq 99.9\%$), and Sb_2O_5 ($\geq 99\%$) (All from Sigma-Aldrich) powders were mixed and calcined at 880°C for 2 h. The prepared powders of CZFO and NKNLS were mixed in 20:80 weight ratio. Mixed powders were pelletized with the diameter of 13 mm and 1~2 mm thick under the pressure of 100 bar. Then the pellets were sintered at $1,070^\circ\text{C}$ for 2 h. X-ray diffraction (XRD: Miniflex600, RIGAKU) using $\text{CuK}\alpha$ ($\lambda=1.5406\ \text{\AA}$) radiation was carried out on prepared samples. The surface morphology of samples was investigated by

scanning electron microscopy (SEM: JEOL-6700F). The magnetic properties were measured with a vibration sample magnetometer (VSM: Model 7404, Lakeshore). For electrical measurements, all samples were polished to 1 mm thickness, and electrode was done with a silver paste. Then, DC field of $3.5\ \text{kV/mm}$ was applied to pole all samples at room temperature for 30 min in silicone oil. Dielectric characteristics were confirmed by using HP 4194A impedance analyzer (Hewlett Packard Co.). Off-resonance and resonance frequency mode ME voltage coefficient were measured by applying DC bias magnetic field H_{ac} of 1 Oe from a Helmholtz coil using a lock-in amplifier (SR860, Stanford Research Systems).

From the XRD patterns in Fig. 1, crystal structures of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0, 0.1$ and 0.2) were investigated in terms of peak shifts. As shown in the Fig. 1(a), a clear spinel structure of CZFO (JCPDS card No. 22-1086) was identified without any secondary peaks by XRD peaks at (311), (440), (220), (400), (222), (422) and (511). The CZFO particles were found to exhibit the particle size below $25\ \mu\text{m}$ with an irregular shape. As shown in Fig. 1(b), the (311) peak at 35.5° shifted with the increase in zinc composition. The phenomenon can be explained by the difference in ionic radius between Co^{2+} ($0.78\ \text{\AA}$) and Zn^{2+} ($0.82\ \text{\AA}$) [16,17].

As shown in Fig. 2, the crystal structure of NKNLS-CZFO

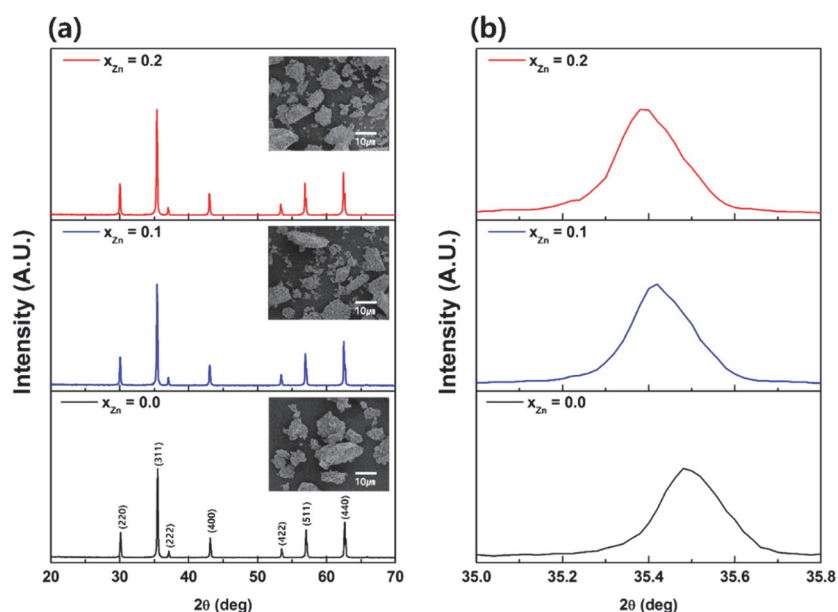


Fig. 1. (a) XRD patterns and inset SEM images of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.0, 0.1$ and 0.2) and (b) shift of (311) peaks.

ME composites were investigated by XRD patterns. After sintering at 1,070°C for 2 h, the NKNLS-CZFO composites with $x_{Zn}=0.0, 0.1$ and 0.2 were found to exhibit a mixed phase consisting of perovskite and spinel as shown in Fig. 2(b). The inset SEM images implies that the ME composites have dense structure.

As shown in Fig. 3, magnetic properties of $Co_{1-x}Zn_xFe_2O_4$ particles $x=0, 0.1$ and 0.2 were investigated using a vibration sample magnetometer (VSM). From Fig. 3(a), the saturation magnetization (M_s) was increased up to 88.7 emu/g ($x=0.1$) from 74.57 emu/g ($x=0$). The result might be due to reported magnetic moments [17,18], i.e., based on Neel's two sublattice model of ferrimagnetism, $CoFe_2O_4$ with the inverse spinel structure is composed of two magnetic sublattices with the tetrahedral A site dominated by Fe^{3+} and the octahedral B site dominated by Co^{2+} . Spins between A and B sublattice are antiparallely aligned by strong super-exchange interactions [19]. The total magnetic moment is influenced by the difference between the magnetic moment values of A and B sublattices. Therefore, the enhancement of magnetization could be attributed to the change in the magnetic moment of B sublattice owing to Zn doping. Figure 3(b) shows the changes in the reduced magnetic coercivity (H_c) from 367.4 Oe to 113.9 Oe with the increase in zinc content. The coercive field is related to the intensity of the magnetic anisotropy produced

by Co^{2+} ions present at the octahedral B site of the spinel structure [20]. Therefore, as the distribution of zinc ions in the cobalt ferrite system increases, the number of cobalt ions located at the octahedral B site decreases, resulting in a decrease in magnetic anisotropy and, consequently, a decrease in the coercive force. Figure 3(c) shows the differential susceptibility ($\chi = \frac{\partial M}{\partial H}$) of the prepared CZFO at room temperature. The CZFO ($x_{Zn}=0.2$) powder with a high Zn content retained the highest differential susceptibility value in the range from 0 to 300 Oe. This is consistent with the expectation that materials with a high susceptibility have low coercivities and vice versa [21].

As shown in Fig. 4, impedance and the corresponding phase angle change were investigated for the magnetoelectric composites of NKNLS-CZFO ($x_{Zn}=0, 0.1$ and 0.2). The ME voltage coefficient can be obtained near the resonance frequency of a piezoelectric phase. The NKNLS-CFO composites exhibited the first peak of phase angle at 320 kHz ($x_{Zn}=0$) and 315 kHz ($x_{Zn}=0.1$ and 0.2).

As shown in Fig. 5, the frequency dependent α_{ME} was investigated at zero dc magnetic field and optimal dc magnetic field. The maximal α_{ME} of 23.15 mV/cm·Oe was achieved at $x_{Zn}=0.1$ at the resonance frequency of 315 kHz and $H_{dc}=0$ Oe. The self-biased ME response is promising, because typical ME composites could not exhibit zero ME response at $H_{dc}=0$

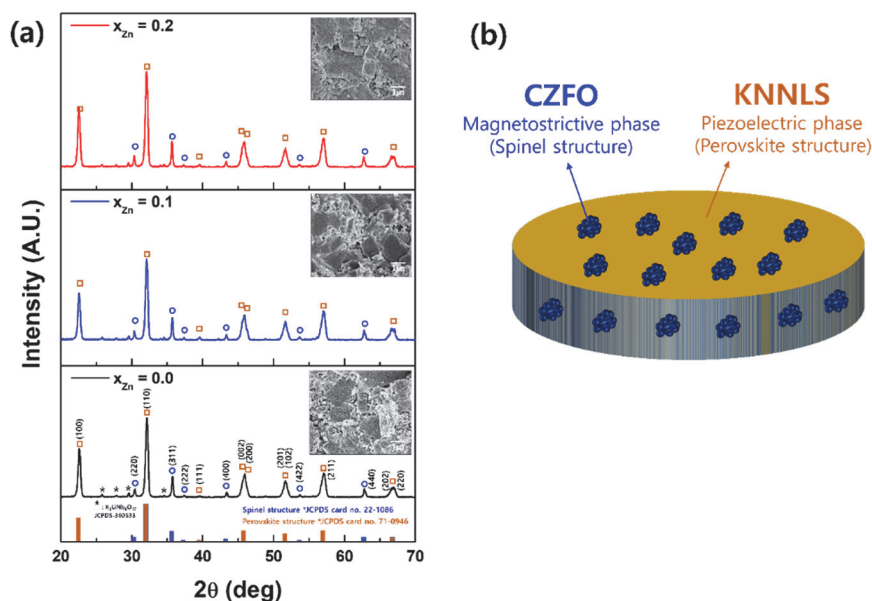


Fig. 2. (a) XRD patterns and (b) schematic illustration of NKNLS-CZFO ($x_{Zn} = 0.0, 0.1$ and 0.2) composites.

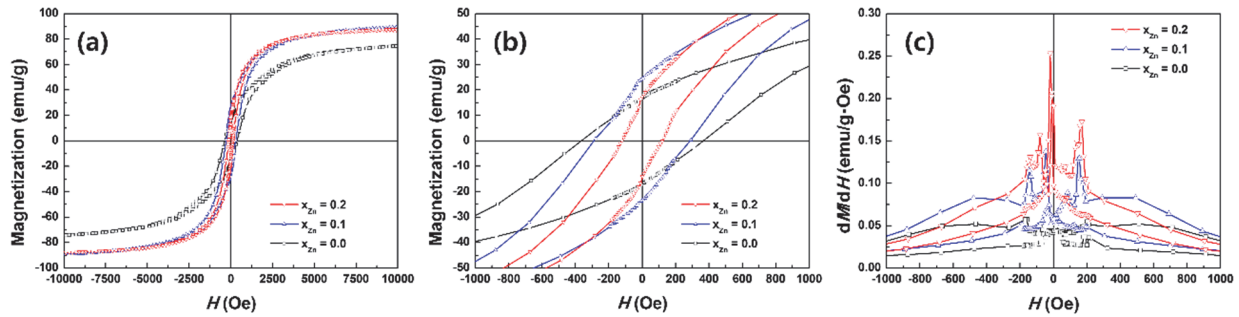


Fig. 3. (a) Magnetic hysteresis loops, (b) magnetic hysteresis loops enlarged to visualize the coercive field region, and (c) magnetic susceptibility ($\chi = \frac{\partial M}{\partial H}$) of CZFO ($x_{Zn}=0.0, 0.1$ and 0.2).

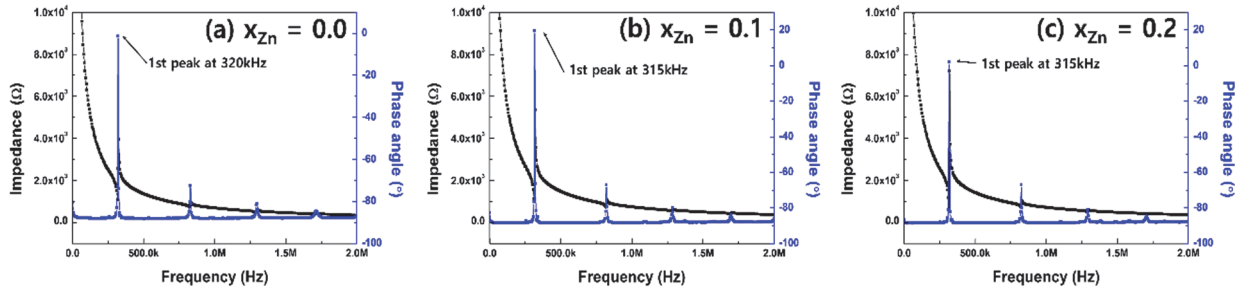


Fig. 4. Impedance and phase angle change in KNLS-CZFO ($x_{Zn}=0, 0.1$ and 0.2).

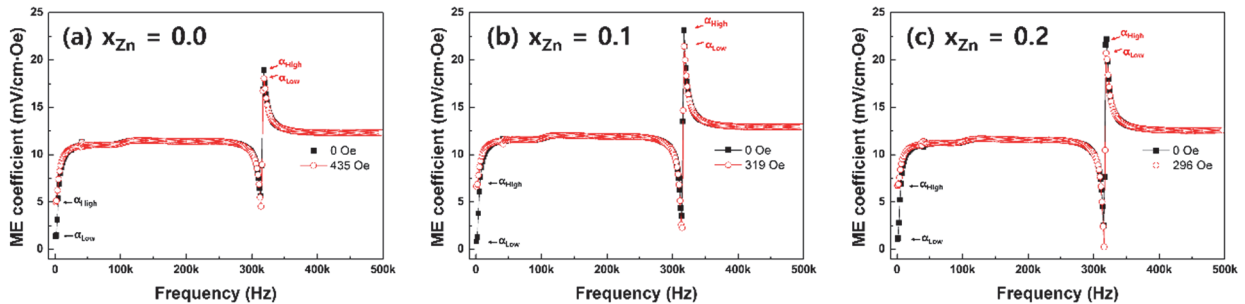


Fig. 5. Frequency dependent magneto-electric voltage coefficient of NKNLS-CZFO ($x_{Zn}=0.0, 0.1$ and 0.2) (the black line was recorded by a frequency sweeping at 0 Oe, and the red line at the optimal magnetic field of 435 Oe, 319 Oe, and 296 Oe).

Oe [22]. This can be explained by the fact that the magnetostrictive phase with a remnant magnetization induces a sufficient deformation to transfer the stress to the piezoelectric phase without applying an external magnetic field. The result illustrated that the self-biased ME composites can be used for magnetic sensors and energy harvesters at off-resonance and resonance frequencies.

In this study, crystal structure, magnetic properties, and frequency dependent ME responses were investigated from

the particulate ME composites of NKNLS-CZFO ($x_{Zn}=0, 0.1$ and 0.2). With the increase in Zn content, the magnetic susceptibility was increased for the self-biased ME responses. The maximal α_{ME} of 23.15 mV/cm·Oe was achieved from the NKNLS-CZFO ($x_{Zn} = 0.1$) composites at resonance frequency of 315 kHz and $H_{dc} = 0$ Oe. From the frequency dependent ME responses, it is clearly described that the self-biased ME composites can be used for the applications both for magnetic sensors and energy harvesters.

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