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Yiping Guo

The Australian National University, Canberra

Yun Liu

The Australian National University, Canberra

Jianli Wang

University of New South Wales, jianli@uow.edu.au

R. L. Withers

The Australian National University, Canberra

Hua Chen

Centre for Advanced Microscopy, The Australian National University.

See next page for additional authors

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Authors

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Giant Magnetodielectric Effect in 0–3 Ni_{0.5}Zn_{0.5}Fe₂O₄-Poly(vinylidene-fluoride) Nanocomposite Films

Yiping Guo,^{†,‡} Yun Liu,^{*,†} Jianli Wang,[§] Ray L. Withers,[†] Hua Chen,[⊥] Lu Jin,[†] and Paul Smith[†]

Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia, State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200240, China, School of Physical, Environmental and Mathematical Sciences, University of New South Wales at Australian Defense Force Academy, ACT 2600, Australia, and Centre for Advanced Microscopy, The Australian National University, Canberra, ACT 0200, Australia

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Multiferroic nanocomposite films, composed of well-dispersed, magnetic Ni_{0.5}Zn_{0.5}Fe₂O₄ (NZFO) nanoparticles (in the size range 10–20 nm) embedded into a poly(vinylidene-fluoride) copolymer matrix host, have been prepared by a modified polymer processing route. The dielectric, ferroelectric, ferromagnetic and magnetodielectric properties of these nanocomposite films have been systematically investigated. The nanocomposite films exhibit low dielectric loss and good ferroelectric character. The magnetodielectric coefficient of the resultant nanocomposite films increases as a function of the NZFO fraction and is almost frequency independent. A giant magnetodielectric coefficient up to 5.1% was obtained at room temperature and under a low magnetic field of 0.3 T. The giant magnetodielectric effect together with low dielectric loss suggests the nanocomposite NZFO films are promising for use in smart multiferroic devices.

1. Introduction

The magnetoelectric (ME) effect (the induction of magnetization by an applied electric field or vice versa) is, potentially, an extremely useful phenomenon with a wide range of device applications. The concept was first proposed by Curie in 1894, on the basis of symmetry considerations,¹ and first experimentally observed in Cr₂O₃.^{2,3} Over more recent times, the ME effect has been observed and investigated in a range of single-phase materials, e.g., Co₃B₇O₁₃Br, Bi₅FeTi₃O₁₅, and LiCoPO₄.^{4–6} Such single-phase magnetoelectric materials, however, remain virtually unused in ME devices due to their low Néel temperatures and the weakness of the ME effect therein.

An alternative approach is to use a composite made of piezoelectric and magnetostrictive materials that ‘talk’ to each other. Over the past few years, multilayer ferroelectric/ferromagnetic thin films^{7–9} as well as bulk or laminate composite materials^{10–16} of this type have attracted growing attention. The ME coefficient is typically two to 3 orders of magnitude higher in ceramic or laminated composites of this type than in single phase materials.^{7,9–15} Laminated composites, however, are difficult to miniaturize and shape as a result of their inherent inhomogeneous toughness. Ceramic composites, on the other hand, are limited by deleterious reactions at the interface regions leading to low resistivities and high dielectric losses >0.1, making such ceramic composites impracticable for device applications.^{15,16}

One way to simplify the preparation process as well as to avoid the problem of interdiffusion between the piezoelectric and magnetostrictive phases is to use component phases that

require significantly lower processing temperatures such as piezoelectric copolymer and magnetic particle composite materials. Some efforts have already been made to form composite materials between piezoelectric copolymers and magnetic particles derived either from conventional solid-state reaction or via sol–gel synthesis.^{17,18} However, the magnetodielectric effect has not been reported yet. Small-sized, well-dispersed, magnetic nanoparticles in a copolymer matrix apparently enhance the mechanical coupling between the magnetic and piezoelectric phases. Much interest has been focused on Ni_{0.5}Zn_{0.5}Fe₂O₄ (NZFO) ferrite as a result of its low anisotropy, high initial magnetic permeability, high electrical resistivity, and relatively low eddy current losses in the high-frequency range.¹⁹ (NZFO) ferrites also exhibit a high Curie temperature (>250 °C) and good magnetostriction properties.^{20,21} In this contribution, we report the preparation of ultrafine NZFO magnetic nanoparticles as well as composite films fabricated by dispersing these NZFO nanoparticles into a poly(vinylidene-fluoride) P(VDF-TrFE) copolymer. The dielectric, ferroelectric, and magnetodielectric properties of the resultant nanocomposite films have been systematically investigated.

2. Experimental Section

The (Ni_{0.5}Zn_{0.5})Fe₂O₄ (NZFO) nanoparticles were synthesized by a hydrothermal process. The analytical grade reagents used as starting materials were nickel(II) chloride hexahydrate [NiCl₂·6H₂O], zinc dinitrate hexahydrate [Zn(NO₃)₂·6H₂O] and iron(III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O]. Ammonium hydroxide [NH₃·H₂O] and ethanolamine served as mineralizers. Stoichiometric NiCl₂·6H₂O, Zn(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O (0.5:0.5:2) reagents were first dissolved in distilled water and then stirred for several minutes to form a transparent solution. Ethanolamine was then dropped slowly into this solution while continuously stirring until precipitation was complete. The obtained products were washed several times with

* Corresponding author. E-mail: yliu@rsc.anu.edu.au.

[†] Research School of Chemistry, The Australian National University.

[‡] State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University.

[§] University of New South Wales at Australian Defense Force Academy.

[⊥] Centre for Advanced Microscopy, The Australian National University.

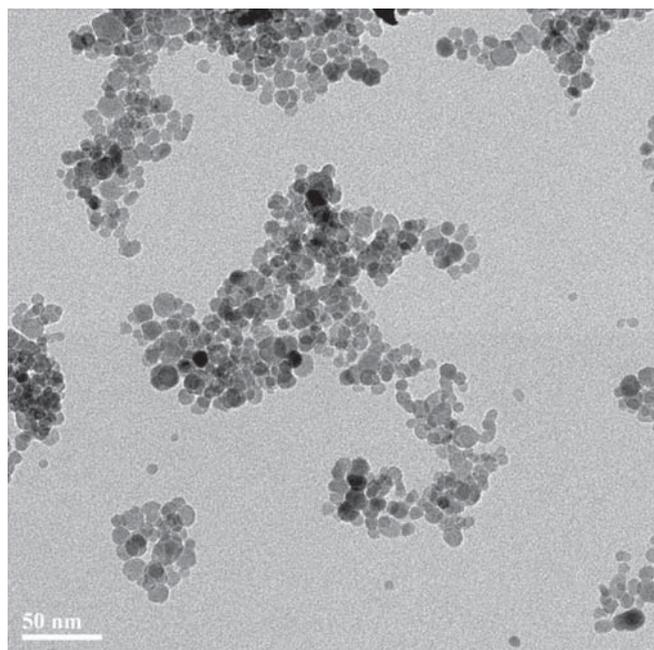


Figure 1. Typical TEM image of NZFO nanoparticles synthesized by a hydrothermal process.

distilled water. $\text{NH}_3 \cdot \text{H}_2\text{O}$ was then added. The final volume of the solution was approximately 40 mL. The resultant mixture was poured into a Teflon vessel which was filled with additional distilled water to 80% of its total volume (50 mL). The vessel was then placed in a stainless steel tank for hydrothermal treatment at 200 °C for 6 h. The obtained products were then washed with distilled water and dried at 60 °C to give a resultant NZFO powder.

The copolymer solution with a VDF/TrFE molar ratio of 75/25 was prepared by dissolving the copolymer powder into *N,N*-dimethylformamide. The synthesized NZFO powder was dispersed into the P(VDF-TrFE) copolymer solution by a combination of ultrasonic vibration (via an ultrasonic bath) and ball milling. The obtained solution was transported into a specially designed molding die that was then heat-treated at 140 °C for 2 h. Crystalline NZFO/P(VDF-TrFE) nanocomposite films with different NZFO weight fractions were thereby obtained. The thickness of the nanocomposite films was $\sim 50\text{--}60 \mu\text{m}$, and the NZFO weight fractions in the copolymer were 5%, 10%, 20%, 30%, and 40%, respectively. The structure and morphology of both the nanopowder and nanocomposite films were investigated by X-ray powder diffraction, transmission electron microscopy (TEM, JEOL JEM-2100F) and field emission scanning electron microscopy (FESEM).

Gold spots were deposited on both sides of the nanocomposite films for electrical measurements using a DC sputter coater. The dielectric properties of the nanocomposite film capacitors were measured using a high-precision LCR meter (HP 4284A), whereas their ferroelectric P - E hysteresis loops were characterized using an aixACCT ferroelectric test unit. The sample was submerged in silicone oil in order to prevent arcing during this process. Magnetic measurements were performed using a Quantum Design SQUID magnetometer. Magnetodielectric measurements were carried out using a HP 4284 LCR meter under an external magnetic field in the range from 0 to 1 T.

3. Results and Discussions

Figure 1 shows a typical low magnification TEM image of the as-synthesized NZFO nanoparticles. Most appear to be

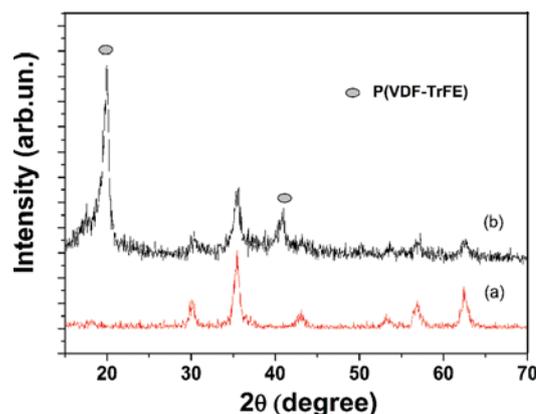


Figure 2. XRD patterns of (a) NZFO nanoparticles and (b) a typical nanocomposite film with a NZFO fraction of 20 wt %.

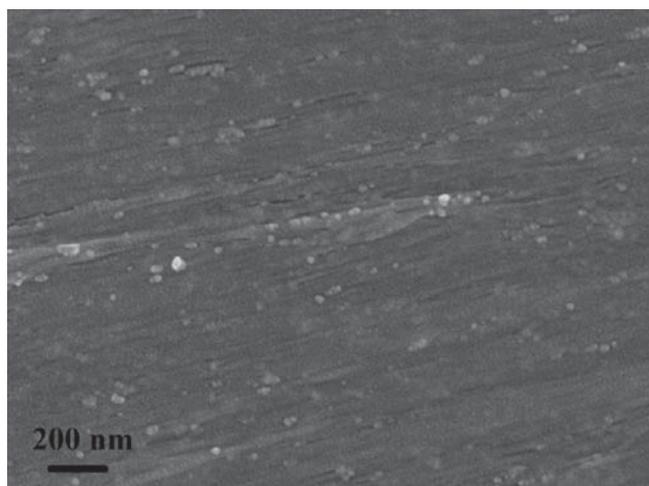


Figure 3. Typical cross-sectional SEM image of a NZFO/P(VDF-TrFE) nanocomposite film with a NZFO fraction of 20 wt %.

spherical with a fairly narrow diameter distribution range between 10 to 20 nm and without any observable aggregation. Monodispersed, ultrafine magnetic nanoparticles of this type embedded into a ferroelectric copolymer host phase could be expected to improve piezoelectric and magnetostrictive coupling as a result of an increased contact area between the magnetic phase and the ferroelectric phase. Figure 2a shows a powder XRD pattern from the NZFO nanoparticles. All of the observed diffraction peaks can be assigned to the expected spinel phase. The observed diffraction peaks are rather broad due to the particle size effect. Figure 2b shows a typical XRD pattern of a resultant film with 20 wt % NZFO. The peaks that do not belong to the NZFO phase originate from the P(VDF-TrFE) copolymer phase, suggesting the coexistence of magnetostrictive NZFO and piezoelectric P(VDF-TrFE) copolymer phases. Figure 3 shows a typical cross-sectional SEM image of the nanocomposite film with 20 wt % NZFO. The bright dots in the image are the NZFO nanoparticles and show that the NZFO particles are rather uniformly dispersed in the copolymer. The morphology (Figure 3), in conjunction with XRD analyses, clearly demonstrates the formation of 0–3 nanocomposite films. The resultant films are very dense with no observable pores in it.

Figure 4 shows the measured room temperature dielectric constant (ϵ_r) and dielectric loss tangent ($\tan \delta$) of the nanocomposite films as a function of frequency over the range 100 Hz to 1 MHz. Note that, with increasing NZFO fraction, both the dielectric constant and loss increase. This can be partially explained by the higher dielectric constant and loss tangent of

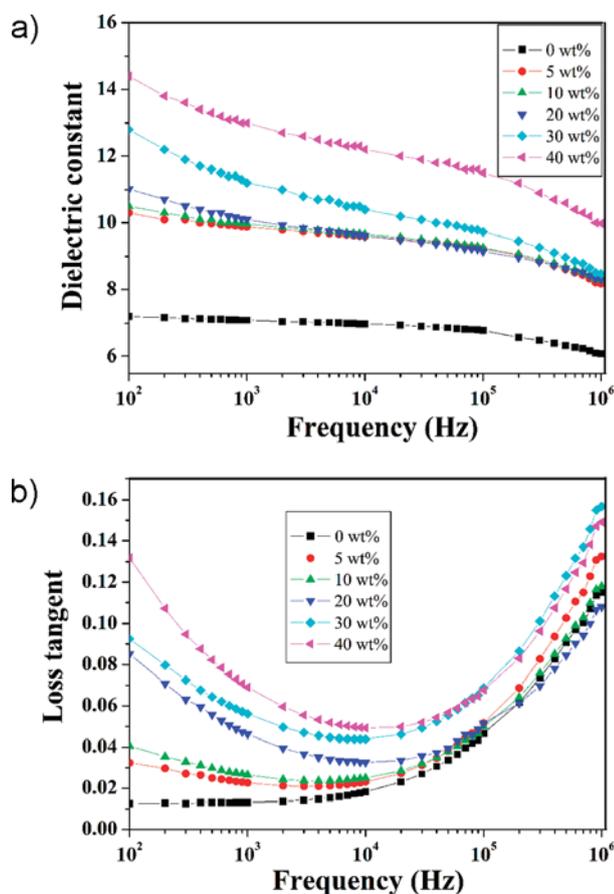


Figure 4. Dielectric constant (a) and loss tangent (b) spectra of NZFO/P(VDF-TrFE) nanocomposite films with different NZFO fractions in the range from 0 to 40 wt %.

the NZFO phase itself relative to those of the copolymer phase and partially by the structural mismatch of the NZFO nanoparticles with the copolymer matrix.²² The latter mismatch is likely to induce localized space charges and Maxwell–Wagner interfacial polarization, thereby making an additional contribution to both the observed dielectric polarization and loss tangent.^{23,24} By contrast with pure copolymer films, the nanocomposite films show relatively stronger frequency dependence within the lower frequency range. The polarization in ferrites such as NZFO originates from the electronic exchange between coexisting Fe^{2+} and Fe^{3+} ions in the *B* site of the spinel phase which cannot follow the applied external electrical field beyond a certain critical frequency and generally decreases monotonically with increasing frequency. As a consequence, the dielectric loss tangent of the nanocomposite decreases as well with increasing frequency. Once the frequency is over 10 kHz, however, the relaxation mechanism associated with the copolymer phase dominates the overall dielectric behavior.²⁵ The dielectric loss tangent of the 0–3 nanocomposite films in the higher-frequency range (above 10 kHz) follows the same trend in loss tangent behavior as the pure copolymer phase (see Figure 4b), suggesting that the observed dielectric behavior of these 0–3 nanocomposite films is not from Maxwell–Wagner interfacial polarization in the higher-frequency range but rather from the intrinsic dielectric properties of the NZFO and copolymer phases.

Figure 5 shows the ferroelectric polarization hysteresis loops of the NZFO/P(VDF-TrFE) nanocomposite films measured at 5 Hz (for films with 1–20 wt % NZFOs) and at 100 Hz (for films with 30 and 40 wt % NZFO). The observed well-defined ferroelectric hysteresis loops demonstrate that the nanocomposite

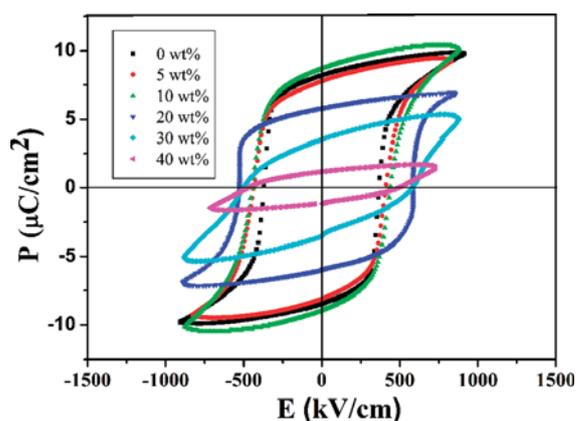


Figure 5. Polarization hysteresis loops of NZFO/P(VDF-TrFE) nanocomposite films measured under an electrical field with an alternating current (AC) frequency of 5 Hz for 0–20 wt % and 100 Hz for 30 and 40 wt % NZFOs.

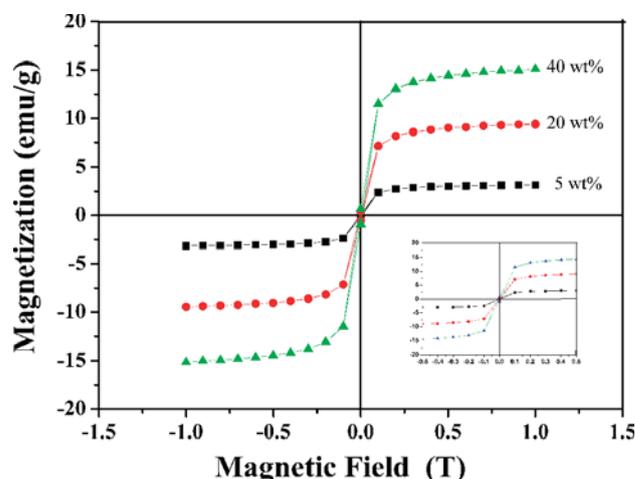


Figure 6. Magnetic hysteresis loops of NZFO/P(VDF-TrFE) nanocomposite films with different NZFO fractions of 5, 20, and 40 wt %. (Insert) Central region on an expanded scale.

films retain good ferroelectric properties even when the NZFO fraction reaches as high as 20 wt %. The remnant polarizations ($2P_r$) are 16.5, 15.8, and 16.6 $\mu\text{C}/\text{cm}^2$ for films with NZFO fractions of 0, 5, and 10%, respectively. On further increase in the NZFO fraction, however, $2P_r$ is 11.9 $\mu\text{C}/\text{cm}^2$ for a nanocomposite film with 20 wt % NZFO. The $2P_r$ drop of 29% by comparison with that of the pure copolymer film is significant. This suggests that there is a critical point for the NZFO fraction. The long-range ordered dipole chains of the copolymer phase are not destroyed as long as the NZFO particle fraction is below this critical point. Beyond this critical point, however, the remnant polarization decreases significantly as shown in Figure 5. When the NZFO fraction is 30 wt %, it becomes virtually impossible to obtain saturated hysteresis loops at an applied frequency of 5 Hz. That is why the hysteresis loops for the 30 and 40 wt % NZFO nanocomposite films were measured at 100 Hz. Furthermore, the coercive fields (E_c) of the nanocomposite films systematically increase with increasing NZFO fraction, presumably because the introduction of the nonferroelectric NZFO phase prevents domain wall movement.

Room temperature magnetic hysteresis loops were measured with the magnetic field applied perpendicular to the surface of the composite films and are shown in Figure 6. The saturation magnetization increases systematically with NZFO content, suggesting that the nonmagnetic copolymer does not prevent the interaction of the magnetic poles of the individual magnetic

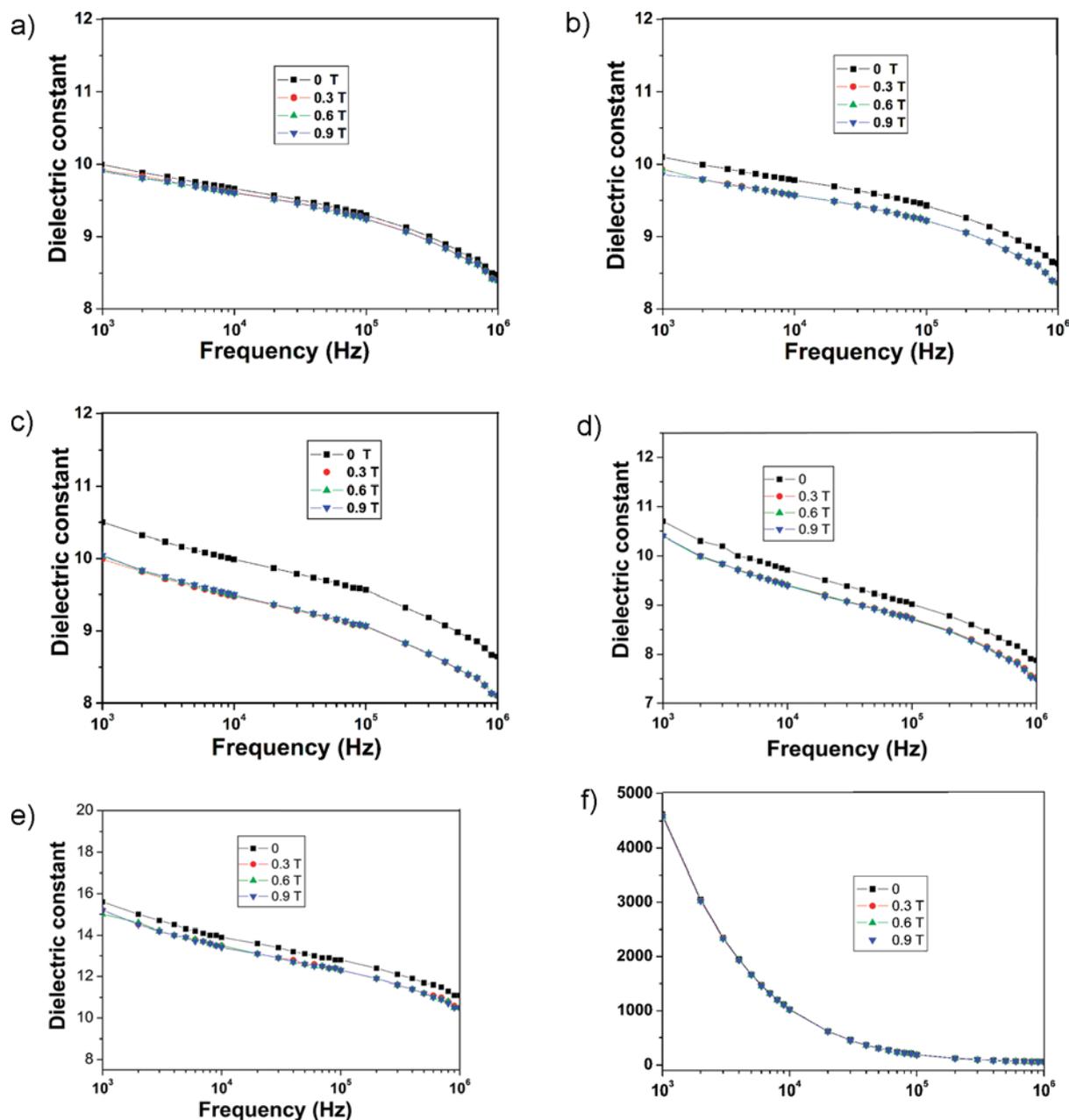


Figure 7. Dielectric constant spectra of NZFO/P(VDF-TrFE) nanocomposite films with respect to applied magnetic field: (a) 5 wt % NZFO, (b) 10 wt % NZFO, (c) 20 wt %, (d) 30 wt %, (e) 40 wt %, and (f) 100 wt % NZFO nanoparticles.

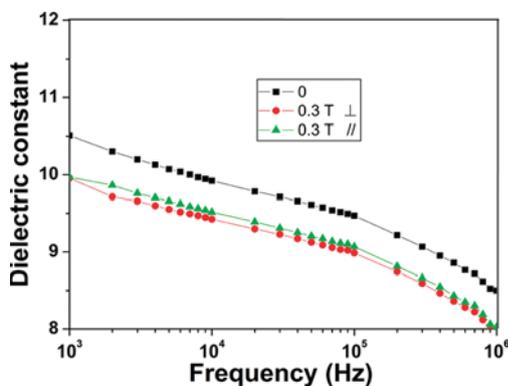


Figure 8. Dielectric constant spectra of the NZFO/P(VDF-TrFE) nanocomposite film with 20 wt % NZFO nanopowder, measured in different magnetic fields with a direction that is parallel (||) or perpendicular (\perp) to the electrical field surfaces.

nanoparticles. As a result, the composite films show saturation under a similar magnetic field no matter what the NFZO fraction is.

The magnetodielectric effect, defined as the induced modulation of the dielectric constant of a material by an applied external magnetic field, has attracted a lot of recent attention due to its potential applications in magnetic field controllable devices or magneto-electric transducers. Efforts to search for materials with a good magnetodielectric effect have focused mainly on ferromagnetic compounds such as ϵ - Fe_2O_3 ,²⁶ double perovskite $\text{La}_2\text{CoMnO}_6$ thin films,²⁷ and terbium iron garnet.²⁸ Such materials, however, always show high dielectric loss and only exhibit a good magnetodielectric effect in the vicinity of the Curie temperature, which makes such materials unsuitable for practical applications.

Figure 7 shows dielectric constant spectra of nanocomposite films measured under different magnetic fields at room tem-

perature, where the NZFO fractions in the films are 5 wt % (a), 10 wt % (b), 20 wt % (c), 30 wt % (d), 40 wt % (e), and 100 wt % (f), respectively. The magnetic field is exerted along the direction perpendicular to the surfaces of the two parallel electrodes of the films. The dielectric constant of the nanocomposite films is significantly changed by an applied magnetic field, demonstrating the occurrence of a magnetodielectric (MD) effect. The different directions between magnetic field and electric field only cause a slight variation in dielectric constant (Figure 8) due to the isotropic magnetostrictive property of the NZFO powder. This small difference between the field parallel and field vertical, however, is evidence of the magnetostrictive/piezoelectric coupling. Pure NZFO ceramic shows a less than 1% variation in dielectric constant (see Figure 7f) and also show an extremely high dielectric loss, similar to other ferromagnetic compounds.^{26–28} Therefore, several factors might contribute to this observed MD effect: the magnetostrictive effect might induce a change in size of the magnetic nanoparticles under an applied magnetic field which in turn would lead to local stresses (or strains) and a consequent change in polarization of the ferroelectric phase due to the piezoelectric effect. Likewise, the magnetostrictive effect might further orient the spins in the magnetic nanoparticles and consequently redistribute charges and dipoles within the polymer matrix, thus leading to a change in polarization. The dielectric constant of the nanocomposite films with higher NZFO fraction has stronger magnetic field dependence since the larger fraction of magnetic particles can create a stronger coupling between the magnetostrictive and piezoelectric phases. From Figure 8, the dielectric spectra characterized under magnetic fields of 0.3, 0.6, and 0.9 T largely overlap each other. This is because the magnetization of the nanocomposite films has already almost saturated at a magnetic field of 0.3 T as observed in Figure 6 where the dielectric constant remains almost unchanged when the applied magnetic field increases from 0.3 T through 0.6 T to 0.9 T. A continued increase in the magnetic field can thus only lead to a minor change in magnetization and consequently has little influence on the measured dielectric constant. The magnetodielectric coupling effect can generally be assessed by a magnetodielectric coefficient (MDC) defined as $MDC(H) = |\epsilon_r(H) - \epsilon_r(0)|/\epsilon_r(0)$. $\epsilon_r(0)$ and $\epsilon_r(H)$ are dielectric constants measured under zero and nonzero magnetic fields, respectively. The MDCs of the nanocomposite films with a NZFO fraction of 5 and 10 wt % are 0.5% and 2.1%, respectively. The MDC increases up to 5.1% for the film having a NZFO fraction of 20 wt %. This value is much higher than those of ferromagnetic materials, e.g., ϵ -Fe₂O₃ (0.3%, 100 K, 6 T), terbium iron garnet (3%, 2 K, 6 T), and Fe₃O₄ (1.0%, 1 K, 0.4 T).^{27–29} Lower MDCs of 3.2% and 2.8% are found for the nanocomposite films with a NZFO fraction of 30 and 40 wt %, presumably due to a weaker piezoelectric response in these films (only unsaturated ferroelectric hysteresis loops were obtained as shown in Figure 5). Single ferromagnetic materials such as NZFO usually only have a good insulating character at very low temperature, at which their intrinsic dielectric properties can be appropriately characterized. Moreover, their magnetodielectric effect, associated with the phase transition or switching of the polarization direction, can only be induced under a high magnetic field.^{27,28} The magnetodielectric effect of such ferromagnetic materials can therefore usually only be observed at a low temperature or under a high magnetic field. In this work, the nanocomposite films show good insulating character at room temperature (Figure 4b) as the NZFO nanoparticles are surrounded and separated by low loss P(VDF-TrFE). This enables the occurrence of the coupling

between magnetostriction and ferroelectric/piezoelectric polarization, resulting in an observable magnetodielectric effect.

The magnetoresistive effect of NZFO can also result in a considerable MD effect where the dielectric permittivity increases while the dielectric loss decreases.³⁰ This type of contribution becomes stronger especially when the dielectric materials do not have good insulating character. In our case, however, the composite films are good insulators, and their dielectric losses are at least 1 order of magnitude lower than that of pure NZFO ceramics. Furthermore, the dielectric permittivity of the composite films decreases with increasing magnetic field (Figure 8), suggesting a combination of magnetoresistivity and the Maxwell–Wagner effect.³⁰ It was also found that the magnetodielectric effect is almost frequency independent, which means the magnetodielectric effect mainly results from the magnetostriction-induced polarization (the Maxwell–Wagner effect) and the contribution of magnetoresistance to the magnetodielectric effect is small.³⁰

4. Conclusions

In conclusion, crystalline ultrafine NZFO nanoparticles with a narrow diameter distribution from 10 to 20 nm were successfully synthesized using a hydrothermal process. They were then homogeneously dispersed in a piezoelectric P(VDF-TrFE) copolymer matrix to form nanocomposite films. The resultant films exhibit low dielectric loss tangents, saturated soft magnetic properties as well as a giant magnetodielectric coupling effect. For instance, a typical magnetodielectric coefficient for the nanocomposite film with a NZFO fraction of 20 wt % is 5.1% under an applied magnetic field of 0.3 T at ambient temperature. We believe that this work provides a promising option for magnetodielectric materials to be applied in smart devices.

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