



Giant magnetoelectric effect of Ni–Mn–Ga/piezopolymer composites tailored by a martensitic transformation

Victor A. L'vov^{a,b}, Pedro Martins^{c,d,*}, N. Pereira^{c,d}, Ander García Díez^e, Hideki Hosoda^f, Volodymyr Chernenko^{e,f,g,h}, Senentxu Lanceros-Mendez^{c,d,g,h}

^a Taras Shevchenko National University of Kyiv, Kyiv, 01601, Ukraine

^b Institute of Magnetism NASU and MESU, Kyiv, 03142, Ukraine

^c Physics Centre of Minho and Porto Universities (CF-UM-UP), Universidade do Minho, 4710-057, Portugal

^d LaPMET - Laboratory of Physics for Materials and Emergent Technologies, Universidade do Minho, 4710-057, Portugal

^e BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, Leioa, 48940, Spain

^f Institute of Innovative Research (IIR), Tokyo Institute of Technology, Yokohama, 226-8503, Japan

^g University of Basque Country (UPV/EHU), Bilbao, 48080, Spain

^h Basque Foundation for Science, IKERBASQUE, Bilbao, 48009, Spain

ARTICLE INFO

Handling Editor: Prof. W. Yang

Keywords:

Magnetoelectrics
Piezoelectrics
Magnetostriiction
Composites
Polymers

ABSTRACT

Polymer-based magnetoelectric (ME) composites, composed of magnetostrictive and piezoelectric phases, in addition to exhibiting an effective coupling between the magnetic and electric orders of the matter, also offer important advantages for the Internet-of-Things, digitalization, and 4.0 revolution environments: light weight, flexibility, wearability, environmental friendliness, printability, and biocompatibility. Nevertheless, their successful implementation on applications such as sensors, actuators, energy harvesters, biomedical devices and spintronics strongly depends on the increase of its ME voltage response.

This work explores, both experimentally and theoretically, the magnetostrictive Ni–Mn–Ga's martensite – austenite phase transformation to shift/tailor/design the ME resonance peak exhibited by Ni–Mn–Ga/P(VDF-TrFE) piezoelectric composites. In the austenite phase, the determined peak value of the ME coefficient of $18.1 \text{ V cm}^{-1} \text{ Oe}^{-1}$ was much higher than the value of $6.05 \text{ V cm}^{-1} \text{ Oe}^{-1}$ obtained for the martensite phase, whereas the estimated theoretically value of magnetoelastic constant in the austenite is much smaller. The ways to further increase the magnetically induced ME response are also outlined.

1. Introduction

Magnetoelectric (ME) materials are a class of materials that exhibit strong coupling between their magnetic and electric properties [1–3]. These materials have the ability to convert magnetic fields into electric fields and vice versa [4–6], making them highly useful for a range of applications in various fields, including dielectrics [7], spintronics [8], data storage [9], sensing [10], energy harvesting [11], and biomedicine [6,12,13]. These materials can be either single-phase (lower ME response and at very low temperatures) or composite materials (high room-temperature ME response) [2], and can be fabricated in a variety of forms, including thin films, bulk crystals, fibres and spheres [6,12,14]. Polymer-based ME materials have gained significant attention in recent years due to their unique combination of properties, including

high ME coupling, flexibility, low density, and the ability to be processed into a wide variety of shapes and sizes [1,15,16]. In particular, the Ni–Mn–Ga/P(VDF-TrFE) composites, introduced in previous reports [17], represent a novel multifunctional ME material type that displays a unique combination of physical properties (structural, piezoelectric, pyroelectric, magnetic, and magnetostructural), originated from the individual properties of Ni–Mn–Ga magnetic shape memory alloy and P(VDF-TrFE) piezoelectric polymer. Moreover, these composites also exhibit synergetic effects that lead to a giant ME effect resulting from the interactions between components [17,18]. Piezoelectricity and pyroelectricity of this material appears as a result of the phase transition from the high-temperature paraelectric phase to the low-temperature ferroelectric phase occurring in the P(VDF-TrFE) copolymer with a 70/30 VDF/TrFE molar ratio at the temperature $T \approx 373 \text{ K}$ [19,20]. The

* Corresponding author. Physics Centre of Minho and Porto Universities (CF-UM-UP), Universidade do Minho, 4710-057, Portugal.

E-mail address: pmartins@fisica.uminho.pt (P. Martins).

<https://doi.org/10.1016/j.compscitech.2023.110101>

Received 4 April 2023; Received in revised form 22 May 2023; Accepted 26 May 2023

Available online 27 May 2023

0266-3538/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

preferred alignment of crystallites and the high degree of crystallinity of P(VDF-TrFE) copolymer lead to a high remnant electric polarization ($\approx 110 \text{ mC m}^{-2}$), which consecutively promotes a mechanical-electrical conversion, materialized in a high electromechanical coupling factor [19,21,22].

Complex magnetostructural properties of the Ni-Mn-Ga/P(VDF-TrFE) composites are closely related to both the ferromagnetic ordering of Ni-Mn-Ga shape memory alloys and the first-order martensitic transformation (MT) from high-temperature cubic phase (austenite) to the low-temperature tetragonal phase (martensite) [23,24]. In the stoichiometric Ni_2MnGa compound the ferromagnetic ordering occurs at the Curie temperature $T_C \approx 375 \text{ K}$ [25], whereas the temperature interval of MT lies well below the room temperature. The latter one can be easily shifted to higher temperatures by slight variations of the chemical composition of the alloy [26–28]. The quasistoichiometric Ni-Mn-Ga alloys are characterized by superelasticity [29–32], giant magnetoelastic [33,34] and magnetostructural responses [35,36], hierarchical micro- and nanostructures [37–39], unusual magnetoresistance [40], and magnetocaloric effect [41–43].

Particulate composites of 0–3 connectivity in a thin film form containing microscopic Ni-Mn-Ga particles distributed with concentration of 10 wt% in the P(VDF-TrFE) piezopolymer have been previously studied [17]. It was found that a superposition of a stationary magnetic field, $\mathbf{H}$, and a weak alternating magnetic field, $\mathbf{h}$, produced an abnormally strong alternating electric field in the Ni-Mn-Ga/P(VDF-TrFE) film, if the frequency of alternating magnetic field was close to the resonant frequency of elastic oscillations of the film. It was revealed that the alternating electric field (ME signal) arose due to the combination of three factors:

- i) elastic straining of polymer due to the volume magnetostriction of Ni-Mn-Ga particles;
- ii) piezoelectric properties of the P(VDF-TrFE) polymer;
- iii) elastic resonance of the composite film caused by the alternating magnetic field.

It can be stated, therefore, that the observed ME signal was a manifestation of magnetically induced piezoelectric effect (MIPE).

In the experiments presented in [17] the vectors of stationary magnetic field, alternating magnetic field and magnetically induced electric field, $\mathbf{E}$, were directed with respect to the film face as shown in Fig. 1(a). The ME resonance was detected at the room temperature, $T_1 = 298 \text{ K}$. At this temperature the Ni-Mn-Ga particles exhibited the martensitic state characterized by a tetragonal crystal lattice and a multi-twinned microstructure. ME coefficient, linearly relating the alternating magnetic field with the resultant electric field, was determined in the frequency range from 0.1 kHz to 200 kHz for a number of stationary magnetic fields. The maximum value of the ME coefficient, $\alpha(f, H)$, was found to be equal to $6.05 \text{ V} \cdot \text{cm}^{-1} \cdot \text{Oe}^{-1}$. This value was measured under

$H=H_1=1.3 \text{ kOe}$ at the resonance frequency $f_{1\text{res}} = 108.2 \text{ kHz}$. To the best of our knowledge, such value exceeds by one order of magnitude the values of the ME coefficient reported before for 0–3 particulate composites [17,44,45].

The theoretical model previously developed [17] quantitatively described an observed ME signal by highlighting the role of the elastic resonance and the volume magnetostriction of Ni-Mn-Ga particles. Moreover, the model showed that the ME signal is proportional to the parameter $F(H) \equiv \chi(H)M(H)$, where $M(H)$ is the magnetization and $\chi(H) = dM(H)/dH$ is the magnetic susceptibility of the film composite. It is well-known that the value of the magnetic susceptibility of a ferromagnetic solid depends on the value of the magnetic anisotropy constant. The uniaxial magnetocrystalline anisotropy constant of the low-symmetry martensitic state of Ni-Mn-Ga alloys is larger by two orders of magnitude than the magnetocrystalline anisotropy constants corresponding to the cubic symmetry of austenite (for more information see review article [46]). The absence of uniaxial magnetocrystalline anisotropy in the austenitic phase, resulting from the martensite–austenite transformation of Ni-Mn-Ga particles, presumes a sharp increase of the magnetic susceptibility and the parameter $F(H)$. This presumption motivated the authors to measure the field-dependence of magnetization and to explore the possibility of significantly increase the maximum value of the ME coefficient of Ni-Mn-Ga/P(VDF-TrFE) films at the temperature $T_2 = 323 \text{ K}$, where the Ni-Mn-Ga particles are in the austenitic phase.

Summing up, the idea of the present research was based on the following considerations. Magnetization of the composite, $M(H)$, is strictly proportional to the magnetization of incorporated Ni-Mn-Ga particles. The theoretical model previously developed [17] showed that the amplitude of the magnetically induced electric signal is proportional to the product of magnetization and magnetic susceptibility of the composite, $F(H)$. The maximum ME signal corresponds to the maximum value of this product, F_{MAX} . As far as F_{MAX} is expected to be much larger for austenitic particles than for martensitic ones, the theoretical model predicts that the martensite – austenite transformation of the particles must amplify the electric signal obtained under resonant conditions. This prediction was explicitly verified experimentally in the present work. As a result, the ME response of $18.1 \text{ V} \cdot \text{cm}^{-1} \cdot \text{Oe}^{-1}$ was measured at the temperature $T_2 = 323 \text{ K}$, the resonance frequency $f_{2\text{res}} \approx 71.8 \text{ kHz}$ and magnetic field $H_2 = 0.485 \text{ kOe}$. It may be advantageous for applications that the maximum ME coefficient is much larger while the magnetic field is much lower in case of the austenitic particles than for the martensitic ones.

2. Experimental

The particulate Ni-Mn-Ga/P(VDF-TrFE) composite film [17] was used for a resumed investigation to get unequivocal evidence of the influence of the phase state (austenite or martensite) of particles on the

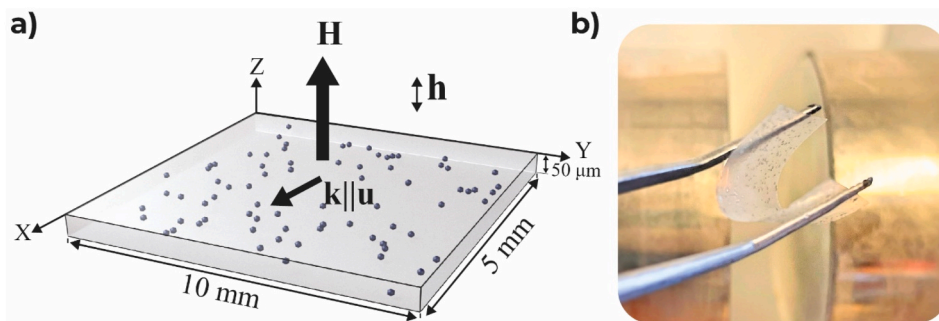


Fig. 1. a) Schematic representation of the experimental specimen, coordinate axes, vectors of stationary and alternating magnetic fields ($\mathbf{H}$ and $\mathbf{h}$, respectively), wave vector $\mathbf{k}$ and displacement vector $\mathbf{u}$, characterizing the magnetically induced elastic wave. b) Photo of the Ni-Mn-Ga/P(VDF-TrFE) film microcomposite in front of the magnet poles.

magnetoelectric response. The composite film with a thickness of 50 μm was prepared by doctor blade, using N,N-Dimethylformamide (DMF) as a polymer solvent, and consisted of the poly(vinylidene fluoride–trifluorethylene) (P(VDF-TrFE)) polymer matrix and irregular shaped $\text{Ni}_{50}\text{Mn}_{28}\text{Ga}_{22}$ (Ni–Mn–Ga) single grain particles with dimensions ranging from 20 to 50 μm uniformly distributed within the polymer matrix. 90 wt% of the polymer and 10 wt% of the magnetic microparticles were added to DMF (8 mL) and mechanically stirred for 2 h with a Teflon mixer in the ultrasound bath to avoid Ni–Mn–Ga agglomeration. The resulting blend was poured onto a very clean glass substrate and held in the oven at 210 $^{\circ}\text{C}$ for 10 min to ensure polymer melting and solvent evaporation. The resulting Ni–Mn–Ga/P(VDF-TrFE) free-standing film microcomposite was obtained by cooling down to ≈ 25 $^{\circ}\text{C}$ (room-temperature) and subsequent peeling off from the glass substrate inside a water container.

The magnetization loops of the film were measured at 298 K and 323 K with the stationary magnetic field applied along the film thickness using a vibrating sample magnetometer (VSM, Oxford Instruments).

The poling of the composite was carried out through corona poling at 10 kV and 120 $^{\circ}\text{C}$ for 120 min with a subsequent cooling to 298 K. The film demonstrated a very stable value of piezoelectric coefficient, $|d_{33}|$, equal to 25 pC N^{-1} , as determined by a wide-Range d_{33} Tester Meter - American Piezo (PA, USA).

The film sample measuring 10 mm $\times$ 5 mm $\times$ 50 μm is schematically shown in Fig. 1. Its faces were clipped between thin gold disks of 2 mm diameter serving as the electrical contacts. Magnetoelectric coefficient, α , was determined at 323 K in the frequency range from 0.1 kHz to 200 kHz under alternative (AC), $h = 0.2$ Oe (controlled by an Agilent 33220A Function/Arbitrary Waveform Generator), and stationary (DC), $H = 458$ Oe (supplied by an EMU-75 electromagnet from SES Instruments – Uttarakhand, India), using a set-up shown in Fig. 2. The AC and DC magnetic fields were superimposed along the thickness direction of the sample, as shown in Figs. 1 and 2.

In the set-up shown in Fig. 2 the magnetically induced elastic wave produced the electrical voltage, which was registered by a Stanford Research Lock-in amplifier (SR530). The temperature of the sample was maintained at 323 K with a Peltier temperature controller.

3. Macroscopic model of magnetically induced piezoelectric response

Physical quantities, which predetermine the characteristics of the ME coefficient $\alpha(f, H)$, can be estimated using the phenomenological

model previously proposed [17]. To explain the essence of these characteristics the model should be briefly described below.

The energy density of the experimental specimen is described by the following equation:

$$U = \frac{1}{2}C_l(\varepsilon_{xx}^2 + \varepsilon_{yy}^2) + \frac{1}{2}C_{tr}\varepsilon_{zz}^2 - \delta_{me}\mathbf{M}^2(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \quad (1)$$

where ε_{ij} are strain tensor components, C_l and C_{tr} are the elastic moduli related to the strain in longitudinal and transversal to the film plane directions, δ_{me} is a phenomenological parameter, which interrelates the volume change caused by the longitudinal elastic waves with the magnetization value. The parameter δ_{me} is a dimensionless magnetoelectric constant if the energy density and magnetization values are measured in erg/cm^3 and Gauss, respectively. In accordance with Fig. 1, the coordinates of the magnetization vector are $M_x = M_y = 0$, $M_z = M(H) + \chi(H)h$. A longitudinal elastic wave is described by the displacement vector $\mathbf{u}$ and wave vector $\mathbf{k} \parallel \mathbf{u}$. It will be argued below that for the resonant wave $k_y = k_z = 0$, and therefore, the strain tensor components are $\varepsilon_{xx} = \partial u_x / \partial x$, $\varepsilon_{zz} = \varepsilon_{yy} = 0$. In this case the linear with respect to h equation for the energy density is

$$U = \frac{1}{2}C_l\varepsilon_{xx}^2 - 2\delta_{me}M(H)\chi(H)h(t)\varepsilon_{xx}. \quad (2)$$

The magnetically induced elastic wave is considered in the model using the complex variables

$$u_x = A \exp\{i(kx - \omega t)\}, h(t) = h_A \exp(-i\omega t), \quad (3)$$

where A is referred to as the complex amplitude of the elastic wave. For the first resonance harmonic the wave vector is equal to π/L , where $L = 5$ mm if $\mathbf{k} \parallel \text{OX}$ (see Fig. 1). A substitution of variables Eq. (5) into the real function $-U$ converts it into the complex function

$$U_c = \frac{1}{2}C_l k^2 u_x^2 + 2ik\delta_{me}M(H)\chi(H)h(t)u_x. \quad (4)$$

The real part of this function is the energy, which is needed to induce the displacement u_x in the unit volume of the film. The Lagrange equation for the Lagrange function

$$\mathcal{L} = \frac{1}{2}\rho \dot{u}_x^2 - U_c \quad (5)$$

can be expressed in the form

$$\ddot{u}_x^2 + 2\gamma\dot{x} + \omega_0^2 u_x = -2ik\delta_{me}M(H)H\chi(H)h(t) / \rho, \quad (6)$$

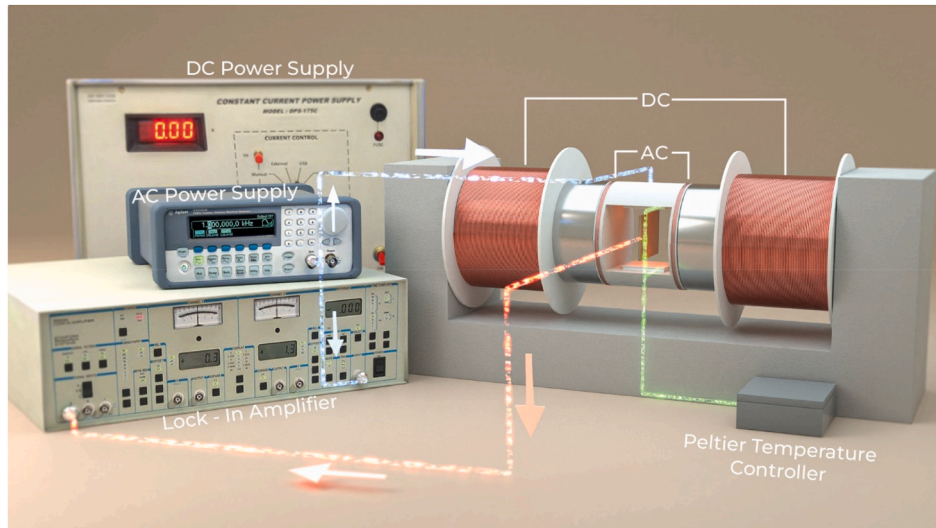


Fig. 2. Schematic representation of the set-up used for the ME measurements, see text for details.

where $\omega_0^2 = C_l k^2 / \rho$, ρ is the mass density of the composite film, $u_x = du_x/dt$, the term $2\gamma u_x$ is added phenomenologically to the Lagrange equation to take into account the energy dissipation, the constant γ is the vibration damping coefficient.

The frequency of resonant elastic wave is expressed by the commonly known relationship $\omega_R = (\omega_0^2 - 2\gamma^2)^{1/2} \approx \omega_0$. The frequency of the first resonance harmonics is close in value to

$$\omega_0 = (\pi/L)(C_l/\rho)^{1/2}. \quad (7)$$

Using Eqs. (3) and (6) the amplitude of the variable elastic strain, induced by the alternating magnetic field, is expressed as

$$\varepsilon_A(H, \omega) = -\frac{\pi^3 \delta_{me} M(H) \chi(H) h_A}{\rho \omega_0^2 L^2} \Lambda(\omega), \quad (8)$$

where

$$\Lambda(\omega) = \frac{\omega_0^2}{[(\omega^2 - \omega_0^2)^2 + 4\gamma^2 \omega^2]^{1/2}}. \quad (9)$$

(For more details see [17]). The function $\Lambda(\omega)$ is equal to unit at $\omega = 0$, tends to zero at $\omega \rightarrow \infty$ and reaches the maximum value $\Lambda_{MAX} = \omega_0 / 2\gamma$ at $\omega = \omega_R$.

The ME coefficient is defined as $\alpha \equiv E_A/h_A$, where E_A is the amplitude of the electric field strength. This coefficient is related to the amplitude of variable strain as

$$\alpha(H, \omega) = \frac{d_{31} C_l \varepsilon_A(H, \omega)}{h_A \varepsilon_0}, \quad (10)$$

where ε_0 is a vacuum permittivity, ε is a relative permittivity of P(VDF-TrFE) polymer. Using Eq. (7) – (10) one can obtain the equation for the maximum values of ME coefficient measured at T_1 , T_2 and H_1 , H_2 :

$$\alpha_{1,2 MAX} = -\frac{d_{31} M(H_{1,2}) \chi(H_{1,2})}{2\pi \varepsilon \varepsilon_0} \left(\frac{\omega_0 \delta_{me}}{\gamma} \right). \quad (11)$$

4. Results

Experimental magnetization loops enable a preliminary estimation of the influence of martensite–austenite transformation of the Ni–Mn–Ga particles on MIPE. These loops are shown in Fig. 3 (a). The $M(H)$ functions measured at $T_1 = 298$ K are strongly different from those obtained at $T_2 = 323$ K. It is obvious that the martensitic transformation proceeding in the Ni–Mn–Ga particles in the temperature range from 305 K to 322 K results in a substantial increase of the magnetic susceptibility of composite. The computations carried out using the average values of magnetization measured for the increasing and decreasing field values (see solid lines in Fig. 3 (a)) show that the increase of

magnetic susceptibility results in a noticeable difference between the functions $F_1(H) = \chi(H, T_1)M(H, T_1)$ and $F_2(H) = \chi(H, T_2)M(H, T_2)$: the maximum value of $F_2(H)$ exceeds the maximum value of $F_1(H)$ by factor 4.67 (see Fig. 3(b)), suggesting that the heating of the composite from 298 K to 323 K must amplify the magnetically induced electric signal by this factor and reduce the magnetic field value, which corresponds to the maximum of the signal, from 1.6 kOe to 0.458 kOe (see the dash-dotted arrows in Fig. 3(b)).

Fig. 4(a) shows the resonance values $\alpha_1 \equiv \alpha(f_{1res}, H)$ and $\alpha_2 \equiv \alpha(f_{2res}, H)$ of the ME coefficients measured at T_1 and T_2 , respectively. This figure and Table 1 facilitate a comparison of the measured maximum values of ME coefficient $\alpha_{1 MAX} \equiv \alpha(f_{1res}, H)$, $\alpha_{2 MAX} \equiv \alpha(f_{2res}, H)$ and correspondent field values, H_1 and H_2 , with the values estimated from magnetization loops. For both temperatures, the difference between the measured and estimated magnetic field values, which correspond to the maximum value of the ME coefficient, is smaller than the step of the applied field. The ratio of the measured maximum values of the ME coefficients $\alpha_{2 MAX}/\alpha_{1 MAX}$ is noticeably smaller than the ratio estimated from magnetization curves as $\alpha_{2 MAX}/\alpha_{1 MAX} \approx F_{2MAX}/F_{1MAX}$. It shows that not only a magnetization process in the Ni–Mn–Ga particles but also a magnetoelastic coupling in the film composite are changed as a result of the martensitic transformation of the particles. This statement is substantiated by the resonance peaks of ME coefficient observed experimentally and computed from Eq. (8) – (10).

Fig. 4 (b) shows the experimental (circles) and theoretical (lines) dependences of the ME coefficient on the frequency of alternating magnetic field obtained at $T = T_2$ and $H = H_2$. The maximum value of the ME coefficient $\alpha_{2 MAX} \approx 18.1 \text{ V} \cdot \text{cm}^{-1} \cdot \text{Oe}^{-1}$ is observed at the frequency $f_{2res} \approx 71.8 \text{ kHz}$, which is the frequency of resonance activation of a standing elastic wave (see [17]). The Inset in Fig. 4(b) shows the experimental and theoretical dependencies of the ME coefficient obtained in [17] at $T = T_1$ and $H = H_1$.

On the one hand, the experimental data presented in Fig. 4 (b) disclose a drastic influence of the martensitic transformation in the Ni–Mn–Ga particles on the elastic resonance, magnetoelastic coupling and MIPE in the composite film as the resonant peak of the ME coefficient appeared to be much narrower and much higher for the austenitic state of particles than for the martensitic one.

On the other hand, the occurrence of ME signal for the austenitic state of particles suggests that MIPE may be observed for ferromagnet/piezopolymer composites even in the case when a ferromagnet does not exhibit martensitic transformation.

To make certain conclusion about the influence of martensitic transformation on the magnetoelasticity of the composite film, the theoretical curve, computed using Eq. (7) – (10), was fitted to the experimental data shown in Fig. 4(b). The experimental values $\varepsilon = 18$ and $d_{31} = 12 \cdot 10^{-12} \text{ C} \cdot \text{N}^{-1}$ [19], $\rho = 2.55 \text{ g} \cdot \text{cm}^{-3}$ [17], and $C_l(T_2) \approx 1.4 \cdot 10^{10} \text{ erg} \cdot \text{cm}^{-3}$ were used for computations. (The elastic modulus C_l was

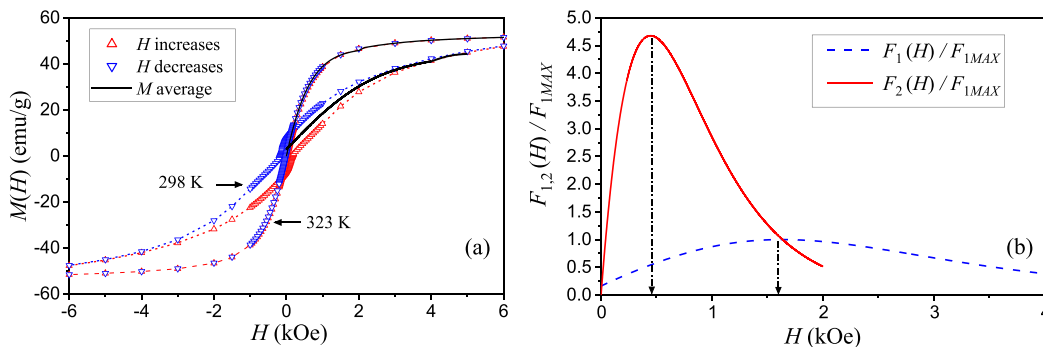


Fig. 3. (a) Magnetization loops measured at 298 K and 323 K (symbols) and used for computations (lines). (b) Normalized values of the functions $F_1(H)$ and $F_2(H)$ computed for 298 K (dashed line) and 323 K (solid line) as explained in the text; the dash-dotted arrows indicate the coordinates of the maximums of these functions.

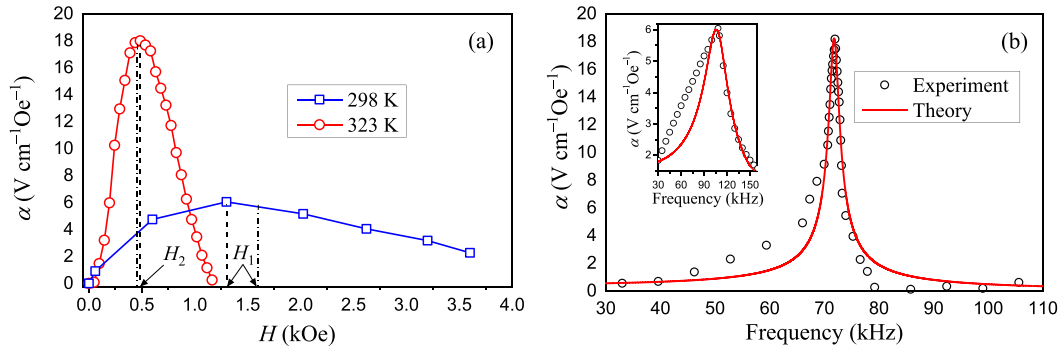


Fig. 4. a) The values of magneto-electric coefficient measured below (squares) and above (circles) the martensitic transformation temperature of particles at the resonance frequency for the different values of the stationary magnetic field. Dashed and dash-dotted lines indicate the observed and estimated from magnetization curves (respectively) values of stationary magnetic field, which correspond to the maximum value of the ME coefficient. b) Magneto-electric coefficient as a function of the frequency of alternating magnetic field measured (circles) and computed (line) for $T_2 = 323$ K, $H_2 = 485$ Oe. Inset shows the experimental and theoretical values obtained in [17] for $T_1 = 298$ K, $H_1 = 1300$ Oe.

Table 1

Magnetic field values marked by the dashed and dash-dotted lines in Fig. 4 (a) and the ratio of maximal values of the ME coefficient.

	H_1 Oe	H_2 Oe	$\alpha_{2MAX}/\alpha_{1MAX}$
Experiment	1300 ^{a)}	485	3.0
Theory	1600	458	4.7

^{a)} Taken from [17].

estimated from the temperature dependence of the Young's modulus reported for P(VDF-TrFE) piezopolymer [48].) The parameter $F_2(H_2) = 0.965 \text{ emu}^2 \cdot \text{g}^{-2} \cdot \text{Oe}^{-1}$ was computed using the $M(H)$ curve shown in Fig. 3(a) and the experimental value $\omega_0 = 2\pi f_{2res}$. To evaluate the dimensionless magnetoelastic constant δ_{me} the experimental values were substituted into Eq. (11) and the relationship $\alpha_{1,2 MAX} = -0.0116(\omega_0 \delta_{me} / \gamma) \text{ V} \cdot \text{cm}^{-1} \cdot \text{Oe}^{-1}$ involving the dimensionless parameter $\omega_0 \delta_{me} / \gamma$ was obtained hence. The values of this parameter determined from the experimental values of $\alpha_{1 MAX}$ and $\alpha_{2 MAX}$ are shown in Table 2. The vibration damping coefficient γ was estimated then by fitting the width of the theoretical ME peak to the experimental points, see Fig. 4(b). The value of magnetoelastic parameter was calculated from $\omega_0 \delta_{me} / \gamma$ and γ values (see Table 2).

The theoretical parameters presented in Table 2 lead to conclusion that the martensite – austenite transformation of Ni-Mn-Ga particles results in a decrease, by one order of magnitude, of both the damping coefficient and dimensionless magnetoelastic constant. The maximal values of the ME coefficient computed using these parameters are close to the experimental value of $6.05 \text{ V} \cdot \text{cm}^{-1} \cdot \text{Oe}^{-1}$, reported in [17] for T_1 , and to the value $18.1 \text{ V} \cdot \text{cm}^{-1} \cdot \text{Oe}^{-1}$, measured at T_2 . Small difference between the theoretical and experimental values of α_{MAX} illustrates the high enough precision of the fitting procedure used for the evaluation of damping coefficient and magnetoelastic constant.

Table 2

Model parameters used for computation of the ME coefficients presented in Fig. 4 (b) for the composite film with austenitic and martensitic (Inset) states of Ni-Mn-Ga particles distributed in the P(VDF-TrFE) polymer.

	$\omega_0 \delta_{me} / \gamma$	γ sec ⁻¹	δ_{me}	α_{MAX} V·cm ⁻¹ ·Oe ⁻¹
T_1	$-2.5 \cdot 10^{4a)}$	$6.8 \cdot 10^{4a)}$	$-2.5 \cdot 10^{4a)}$	$6.2^{b)}$
T_2	$-1.6 \cdot 10^5$	$5.64 \cdot 10^3$	$-2 \cdot 10^3$	$18.3^{b)}$

^{a)} Taken from [17].

^{b)} Computed for the estimated values H_2 (see Table 1).

5. Discussion

As it was shown in [17], a substitution of the mass density of composite film, resonance frequency of elastic wave $\omega_0 = 2\pi f_{1res}$ and elastic modulus $C_l = 12 \cdot 10^{10} \text{ erg} \cdot \text{cm}^{-3}$ into Eq. (7) results in the value $L \approx 1$ cm. For the wave with the wave vector perpendicular to the composite film plane the resonance frequency is higher by the factor L/l_0 , where l_0 is the film thickness. The experimental value of Young's modulus of P(VDF-TrFE) polymer decreases on heating being approximately equal to 2.1 GPa and 1.4 GPa for the temperatures T_1 and T_2 , respectively [48]. Accepting these values for C_l and substituting them into Eq. (7), one can obtain the values $L_1 = 0.42$ cm and $L_2 = 0.52$ cm, respectively. Both values correspond to the length $\lambda \approx 5$ mm of standing wave with the wave vector oriented as shown in Fig. 1.

The reasons of the influence of the martensite – austenite transformation of Ni-Mn-Ga particles on the resonant peak width and the magnetoelastic coupling are complex, although some assumptions can be made. A drastic difference between the width of resonant peaks observed in the martensitic and austenitic states of particles (see peaks in Fig. 4 (b) and in the Inset) can be explained, in principle, by the fundamental difference in their microstructures entailing a strong difference in the magnetic properties inherent to these states. The difference between the estimated values of magnetoelastic constants (Table 2) suggests that the volume magnetostriction of Ni-Mn-Ga particles is not the only reason of the elastic straining of polymer by the alternating magnetic field but some other specific microscopic mechanisms of magnetoelastic coupling may be encountered in the piezopolymer containing an ensemble of small ferromagnetic particles, such as mechanisms related to its semicrystalline nature and specific microstructure [49].

The results and findings of the present work allow to foresee some MM/P(VDF-TrFE) composite with even larger ME coefficient than that shown in Fig. 4 (b) on the conditions that an anticipated magnetic material (MM) exhibits both a high magnetic susceptibility and a large magnetostriction. To develop such composite material, further investigations aiming to clarify the microscopic mechanisms of magnetoelastic coupling in the particulate Ni-Mn-Ga/P(VDF-TrFE) material are necessary. Additionally, the magnetically induced elastic resonance in such hypothetical MM/P(VDF-TrFE) and studied here Ni-Mn-Ga/P(VDF-TrFE) composites is promising for applications since such magneto-electric materials with wide resonance peaks are suitable for energy harvesting devices and those with the narrow resonance peaks are promising for sensing. Furthermore, the particulate composite materials with MM magnetostrictive particles showing structural, magnetic or magnetostructural phase transformations may be advantageous for their implementation in devices operating by a “temperature switching”

of their functional characteristics.

6. Conclusions

This study reports a giant magnetoelectric response, at the resonance frequency, of the particulate Ni–Mn–Ga/P(VDF-TrFE) piezoelectric composite suitable for magnetic energy harvesting, sensing and actuation once the magnetoelectric coefficient is three orders of magnitude higher than the traditionally observed in 0–3 composites. Additionally, it was found that different Ni–Mn–Ga phases led to different ME performances of the Ni–Mn–Ga/P(VDF-TrFE) microcomposites: in the austenite phase of particles, a peak value of the ME coefficient of $18.1 \text{ V cm}^{-1} \text{ Oe}^{-1}$ appeared to be much higher than the value of $6.05 \text{ V cm}^{-1} \text{ Oe}^{-1}$ obtained for the martensite phase. Such experimental observation is explained by the lower value of magnetoelastic constant value in the austenite theoretically determined (-2.5×10^4 for the martensite phase and -2×10^3 for the austenite phase).

The theoretical part of this work opens experimental doors for the tailoring of the magnetic properties of the magnetostrictive fillers in the piezopolymers for specific applications, such as sensors (narrow resonance peaks), energy harvesters (wide resonance peaks) and temperature switches/actuators (martensite-austenite phase transition).

Author statement

All authors participated in the research and writing of the paper. All authors approve/agree with this submission.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The financial supports from the Basque Government Department of Education [project IT1479-22], the Tokyo Tech Fund [ASUNARO Grant], and the Japan Society for the Promotion of Science (JSPS) (projects KAKENHI 20K20544, 22H00256) are greatly acknowledged.. V.C. is grateful for support from World Research Hub (WRH) Program of International Research Frontiers Initiative, Tokyo Institute of Technology. V.L. is grateful to BCMaterials for supporting his research visit. This study forms part of the Advanced Materials program and was supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by the Basque Government under the IKUR and the ELKARTEK program. A.G.D thank the Basque Government for funding under an FPI grant PRE_2020_1_0201. The authors also thank the Portuguese Foundation for Science and Technology (FCT) for funding in the framework of the Strategic Funding UID/FIS/04650/2020, the project 2022.05540.PTDC and the contract under the Stimulus of Scientific Employment CEECIND/03975/2017.

References

- [1] P. Martins, J.S. Nunes, J. Oliveira, N. Perinka, S. Lanceros-Mendez, Spray-printed Magnetoelectric Multifunctional Composites *Composites Part B: Engineering*, 2020, p. 187.
- [2] R. Brito-Pereira, C. Ribeiro, S. Lanceros-Mendez, P. Martins, Magnetoelectric response on terfenol-D/P(VdF-TrFE) two-phase composites, *Compos. B Eng.* 120 (2017) 97–102.
- [3] C.S. Lehmann Fernández, N. Pereira, S. Lanceros-Méndez, P. Martins, Evaluation and optimization of the magnetoelectric response of $\text{CoFe}_2\text{O}_4/\text{poly}(\text{vinylidene fluoride})$ composite spheres by computer simulation, *Compos. Sci. Technol.* 146 (2017) 119–130.
- [4] R. Gao, Q. Zhang, Z. Xu, Z. Wang, G. Chen, X. Deng, C. Fu, W. Cai, A comparative study on the structural, dielectric and multiferroic properties of $\text{Co}_0.6\text{Cu}_0.3\text{Zn}_0.1\text{Fe}_2\text{O}_4/\text{Ba}_0.9\text{Sr}_0.1\text{Ti}_0.9\text{O}_3$ composite ceramics, *Compos. B Eng.* 166 (2019) 204–212.
- [5] C.S. Lehmann Fernández, N. Pereira, P. Martins, S. Lanceros-Méndez, Theoretical Design of High-Performance Polymer-Based Magnetoelectric of Fibrillar Structures *Composites Science and Technology* 155 (2018) 126–136.
- [6] P. Martins, C.S.L. Fernandez, D. Silva, S. Lanceros-Méndez, Theoretical Optimization of Magnetoelectric Multilayer Laminates *Composites Science and Technology*, 2021, p. 204.
- [7] P. Martins, D. Silva, M.P. Silva, S. Lanceros-Mendez, Improved magnetodielectric coefficient on polymer based composites through enhanced indirect magnetoelectric coupling, *Appl. Phys. Lett.* 109 (2016).
- [8] J.S. Moodera, Magnetoelectric coupling lights up spintronics path: lithium battery ideas to tune magnetism, *Matter* 4 (2021) 3372–3373.
- [9] M.K. Sharif, M.A. Khan, M. Junaid, M.J. Akhter, Enhanced magnetic and ferroelectric properties of K–Hf substituted Bifeo3 Multiferroics for magnetoelectric data storage applications, *Ferroelectrics* 599 (2022) 168–177.
- [10] N. Pereira, A.C. Lima, V. Correia, N. Perinka, S. Lanceros-Mendez, P. Martins, Magnetic Proximity Sensor Based on Magnetoelectric Composites and Printed Coils *Materials*, 13, 2020.
- [11] R. Brito-Pereira, C. Ribeiro, N. Pereira, S. Lanceros-Mendez, P. Printed Martins, Multifunctional magnetically activated energy harvester with sensing capabilities, *Nano Energy* 94 (2022).
- [12] T. Zheng, Z. Yue, G.G. Wallace, Y. Du, P. Martins, S. Lanceros-Mendez, M. J. Higgins, Local probing of magnetoelectric properties of $\text{Pvdf}/\text{Fe}_3\text{O}_4$ electrospun nanofibers by piezoresponse force microscopy, *Nanotechnology* 28 (2017).
- [13] B. Hermenegildo, C. Ribeiro, L. Pérez-Álvarez, J.L. Vilas, D.A. Learmonth, R. A. Sousa, P. Martins, S. Lanceros-Méndez, Hydrogel-based magnetoelectric microenvironments for tissue stimulation, *Colloids Surf. B Biointerfaces* 181 (2019) 1041–1047.
- [14] P. Martins, S. Lanceros-Méndez, Polymer-based magnetoelectric materials: to Be or not to Be, *Appl. Mater. Today* 15 (2019) 558–561.
- [15] Y. Yao, S. Jin, D. Wang, J. Wang, D. Li, X. Lv, Q. Shu, Flexible magnetoelectric coupling nanocomposite films with multilayer network structure for dual-band emi shielding, *Compos. Sci. Technol.* (2022) 222.
- [16] S. Reis, M.P. Silva, N. Castro, V. Correia, J.G. Rocha, P. Martins, A. Lasheras, J. Gutierrez, S. Lanceros-Mendez, Electronic optimization for an energy harvesting system based on magnetoelectric metglas/poly(vinylidene fluoride)/metglas composites, *Smart Mater. Struct.* 25 (2016).
- [17] P. Martins, A.C. Lima, V.A. L'vov, N. Pereira, P. Sratong-on, H. Hosoda, V. Chernenko, S. Lanceros-Mendez, In a search for effective giant magnetoelectric coupling: Magnetically induced elastic resonance in Ni–Mn–Ga/P(VDF-TrFE) composites, *Appl. Mater. Today* 29 (2022) 101682.
- [18] X. Wang, J. Zhang, X. Xia, C. Fang, G.J. Weng, Nonlinear magnetoelectric effects of polymer-based hybrid magnetoelectric composites with chain-like Terfenol-D/Epoxy and PvdF multilayers, *Compos. Sci. Technol.* (2021) 216.
- [19] P. Martins, A.C. Lopes, S. Lanceros-Mendez, Electroactive phases of poly (vinylidene fluoride): determination, processing and applications, *Prog. Polym. Sci.* 39 (2014) 683–706.
- [20] J. Niu, C. Li, Q. Fang, M. Fan, X. Liu, P. Hu, Large mechanical-to-electric output originated from optimized configuration in P(VdF-TrFE)-Based nanocomposite fibrous membrane as wearable nanogenerator, *Compos. Sci. Technol.* (2022) 220.
- [21] C. Ribeiro, C.M. Costa, D.M. Correia, J. Nunes-Pereira, J. Oliveira, P. Martins, R. Gonçalves, V.F. Cardoso, S. Lanceros-Méndez, Electroactive poly(vinylidene fluoride)-based structures for advanced applications, *Nat. Protoc.* 13 (2018) 681–704.
- [22] S. Wang, H.Q. Shao, Y. Liu, C.Y. Tang, X. Zhao, K. Ke, R.Y. Bao, M.B. Yang, W. Yang, Boosting piezoelectric response of PvdF-trfe via Mxene for self-powered linear pressure sensor, *Compos. Sci. Technol.* (2021) 202.
- [23] P. Lázpita, J.M. Barandiarán, J. Gutiérrez, C. Mondelli, A. Sozinov, V. A. Chernenko, Polarized neutron study of Ni–Mn–Ga alloys: site-specific Spin density affected by martensitic transformation, *Phys. Rev. Lett.* 119 (2017).
- [24] F. Nilsén, I. Aaltio, S.P. Hannula, Comparison of magnetic field controlled damping properties of single crystal Ni–Mn–Ga and Ni–Mn–Ga polymer hybrid composite structures, *Compos. Sci. Technol.* 160 (2018) 138–144.
- [25] P.J. Webster, K.R.A. Ziebeck, S.L. Town, M.S. Peak, Magnetic order and phase transformation in Ni_2MnGa , *Phil. Mag. B* 49 (1984) 295–310.
- [26] V.A. Chernenko, E. Cesari, V.V. Kokorin, I.N. Vitenko, The development of new ferromagnetic shape memory alloys in Ni–Mn–Ga system, *Scripta Metall. Mater.* 33 (1995) 1239–1244.
- [27] X. Jin, D. Bono, R.C. O'Handley, S.M. Allen, T.Y. Hsu, Magnetic field effects on strain and resistivity during the martensitic transformation in Ni–Mn–Ga single crystals, *J. Appl. Phys.* 93 (2003) 8630–8632.
- [28] N. Lanska, O. Söderberg, A. Sozinov, Y. Ge, K. Ullakko, V.K. Lindroos, Composition and temperature dependence of the crystal structure of Ni–Mn–Ga alloys, *J. Appl. Phys.* 95 (2004) 8074–8078.
- [29] V.A. Chernenko, V. L'vov, J. Pons, E. Cesari, Superelasticity in high-temperature Ni–Mn–Ga alloys, *J. Appl. Phys.* 93 (2003) 2394–2399.
- [30] V.A. L'vov, A. Kosogor, J.M. Barandiarán, V.A. Chernenko, Destabilization of Ni–Mn–Ga martensite: experiment and theory, *Acta Mater.* 60 (2012) 1587–1593.
- [31] V.A. Chernenko, E. Villa, D. Salazar, J.M. Barandiarán, Large tensile superelasticity from intermartensitic transformations in $\text{Ni}_{49}\text{Mn}_{28}\text{Ga}_{23}$ single crystal, *Appl. Phys. Lett.* 108 (2016).

- [32] Z. Ding, D. Liu, Q. Qi, J. Zhang, Y. Yao, Y. Zhang, D. Cong, J. Zhu, Multistep superelasticity of Ni-Mn-Ga and Ni-Mn-Ga-Co-Cu microwires under stress-temperature coupling, *Acta Mater.* 140 (2017) 326–336.
- [33] V.A. Chernenko, V.A. L'vov, Magnetoelastic nature of ferromagnetic shape memory effect, *Mater. Sci. Forum* 583 (2008) 1–20.
- [34] O. Heczko, Magnetoelastic coupling in Ni-Mn-Ga magnetic shape memory alloy, *Mater. Sci. Forum* 635 (2010) 125–130.
- [35] V.A. L'vov, V.A. Chernenko, J.M. Barandiaran, Magnetic shape memory materials with improved functional properties: scientific aspects, in: A. Zhukov (Ed.), *Novel Functional Magnetic Materials: Fundamentals and Applications*, Springer International Publishing, Cham, 2016, pp. 1–40.
- [36] V. Chernenko, Magnetostrictive Ni-Mn-based heusler alloys, in: A.-G. Olabi (Ed.), *Encyclopedia of Smart Materials*, Elsevier, Oxford, 2022, pp. 160–176.
- [37] P. Müllner, A.H. King, Deformation of hierarchically twinned martensite, *Acta Mater.* 58 (2010) 5242–5261.
- [38] L. Straka, H. Hänninen, N. Lanska, A. Sozinov, Twin interaction and large magnetoelasticity in Ni-Mn-Ga single crystals, *J. Appl. Phys.* 109 (2011).
- [39] P. Müllner, Twinning stress of type I and type II deformation twins, *Acta Mater.* 176 (2019) 211–219.
- [40] V.O. Golub, V.A. Chernenko, A. Apolinario, I.R. Aseguinolaza, J.P. Araujo, O. Salyuk, J.M. Barandiaran, G.N. Kakazei, Negative magnetoresistance in nanotwinned Ni-Mn-Ga epitaxial films, *Sci. Rep.* 8 (2018).
- [41] V.A. Chernenko, V.A. L'vov, E. Cesari, J.M. Barandiaran, Fundamentals of magnetocaloric effect in magnetic shape memory alloys, *Handb. Magn. Mater.* 28 (2019) 1–45.
- [42] S. Fabbri, J. Kamarad, Z. Arnold, F. Casoli, A. Paoluzi, F. Bolzoni, R. Cabassi, M. Solzi, G. Porcari, C. Pernechele, F. Albertini, From direct to inverse giant magnetocaloric effect in Co-doped Ni-Mn-Ga multifunctional alloys, *Acta Mater.* 59 (2011) 412–419.
- [43] S. Glock, L.P. Canal, C.M. Grize, V. Michaud, Magneto-mechanical actuation of ferromagnetic shape memory alloy/Epoxy composites, *Compos. Sci. Technol.* 114 (2015) 110–118.
- [44] X. Liang, A. Matyushov, P. Hayes, V. Schell, C. Dong, H. Chen, Y. He, A. Will-Cole, E. Quandt, P. Martins, J. McCord, M. Medarde, S. Lanceros-Mendez, S. Van Dijken, N.X. Sun, J. Sort, Roadmap on Magnetoelectric Materials and Devices *IEEE Transactions on Magnetics* 57 (2021).
- [45] N. Pereira, A.C. Lima, S. Lanceros-Mendez, P. Magnetoelectrics Martins, Three centuries of research heading towards the 4.0 Industrial revolution, *Materials* 13 (2020).
- [46] V. L'vov, V. Chernenko, Magnetic anisotropy of ferromagnetic martensites, *Mater. Sci. Forum* 684 (2011) 31–47.
- [48] J. Hafner, M. Teuschel, M. Schneider, U. Schmid, Origin of the strong temperature effect on the piezoelectric response of the ferroelectric (Co-)Polymer P(Vdf 70 -trfe 30), *Polymer* 170 (2019) 1–6.
- [49] M.C. García-Gutiérrez, A. Linares, I. Martín-Fabiani, J.J. Hernández, M. Soccio, D. R. Rueda, T.A. Ezquerro, M. Reynolds, Understanding crystallization features of P (Vdf-Trfe) copolymers under confinement to optimize ferroelectricity in nanostructures, *Nanoscale* 5 (2013) 6006–6012.
- [47] P. Sratong-on, V.A. Chernenko, J. Feuchtwang, H. Hosoda, Magnetic field-induced rubber-like behavior in Ni-Mn-Ga particles/polymer composite, *Sci. Rep.* 9 (2019).