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Review Article

Current Status of Magnetoelectric Composite Thin/Thick Films

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Here we review the current status of magnetoelectric (ME) multiferroics and ME composite thin/thick films. The magnitude of ME coupling in the composite systems is dependent upon the elastic coupling occurring at the interface of piezoelectric and magnetostrictive phases. The multiferroic ME films in comparison with bulk ME composites have some unique advantages and show higher magnitude of ME response. In ME composite films, thickness of the films is one of the important factors to have enough signal. However, most of all reported ME nanocomposite structured films in literature are limited in overall thickness which might be related to interface strain resulting from difference in thermal expansion mismatch between individual phases and the substrate. We introduced noble ME composite film fabrication technique, aerosol deposition (AD) to overcome these problems. The success in AD fabrication and characterization of ME composite films with various microstructure such as 3-2, 2-2 connectivity are discussed.

1. Introduction

The progress of human civilization has been strongly influenced by the progress in the field of materials science. Materials science is an extremely interdisciplinary subject involving branches such as Physics, Chemistry, Engineering, Biology, and so forth. Understanding the basic aspects of a variety of materials such as their structure and properties is the key issue in materials science. Based upon the fundamental understanding of structure-property relationship, new materials with enhanced performance are currently being developed. A material is generally said to be functional if it possesses a physical property that is utilizable in applications. Among the various classes of materials, *functional materials*, which interest lies in their physical properties, occupy a particularly important place in our lives, as they allow, for example, for the design of many electronic devices we use them on a daily basis. Especially, the rapid improvement of mobile devices requires smaller components, which can be obtained by designing multifunctional materials which possess several properties as ferromagnetism, ferroelectricity.

Magnetic and ferroelectric materials are present in the wide range of modern science and technology. Ferromagnetic materials with switchable magnetization M driven by an external magnetic field H are essential for data-storage industries. Also, the sensing manufacturing trusts profoundly on ferroelectric materials with spontaneous polarization P reversible upon an external electric field E because most ferroelectrics are ferroelastics or piezoelectric with spontaneous strain. This allows such materials to be used for various applications where elastic energy could be converted in to electric energy and vice versa. Furthermore, ferroelectric materials are also used for data storage in random-access memories (FeRAMs).

This review article is mainly concentrated on the current status and ongoing research activity of a new class of materials known as magnetoelectric (ME) multiferroic composites, which are simultaneously ferromagnetic and ferroelectric within one material.

Multiferroic materials exhibit at least two of the “ferroic” properties—ferroelectricity, ferromagnetism, ferroelasticity, and ferrotoroidicity—in the same phase [1]. These ferroic materials have all the potential applications of ferromagnetic and ferroelectric materials. In addition, there could be a possibility of new range of application if coupling can be achieved between different kinds of ferroic orders, for example, ferroelectricity ferromagnetism. The possibility to control magnetization and/or polarization by an electric field and/or magnetic field; that is, ME effect allows additional degree of freedom in multifunctional device design. The ME effect is defined as an induced electric polarization (P) of a material with an applied magnetic field (H), that is, direct effect or an induced magnetization (M) with an external electric field (E), that is, converse effect [2, 3]

$$\Delta P = \alpha\ \Delta H \text{ or } \Delta E = \alpha_E\ \Delta H[\text{direct ME effect}],$$
$$\Delta M = \alpha\ \Delta E[\text{converse ME effect}], \quad (1)$$

where $\alpha(\alpha_E)$ is the ME voltage coefficient. This means that the electric polarization/magnetization can be modified by the application of a magnetic field/electric field of the materials via the ME coupling.

2. Historical Background of ME Composites

The history of the ME effect dates back to as early as 1894, when Curie stated that "*Les conditions de symétrie nous montrent qu'il pourrait se faire qu'un corps à molécules dissymétriques se polarise diélectriquement lorsqu'on le place dans un champ magnétique.... Et peut-être magnétiquement lorsqu'on le place dans un champ électrique.*" (The applications of symmetry conditions provide us that a body with an asymmetric molecule gets electrically polarized when placed in a magnetic field.... And perhaps magnetically when placed in an electric field) [4]. However, no further work was done until 1958 when Landau and Lifshitz proved the possibility of the ME effect in certain crystals on the basis of the crystal symmetry [5]. The symmetry argument was applied by Dzyaloshinskii (1960) to antiferromagnetic Cr_2O_3, and it was suggested that the ME effect could be seen in Cr_2O_3 [6]. This was followed by experimental confirmation by Astrov (1960) who measured the electrically induced ME effect in Cr_2O_3 in the temperature range of 80 to 330 K [7]. Since then there have been many papers reporting observations and measurements of the ME effect in single crystals, polycrystalline or powdered specimens of Cr_2O_3 as well as in many other materials [8–21]. However, with the exceptions of one or two, almost all exhibit the ME effect at low temperatures, much below the room temperature, since they have low Néel or Curie temperatures. The ME coefficient drops to zero as the temperature reaches the transition temperature. Because of this, it is difficult to make use of the ME effect in the single-phase materials for device applications.

From the viewpoint of material constituents, multiferroic ME materials can essentially be divided into two types: single phase [22, 23] and composite [24, 25]. However, these single-phase multiferroic materials only had coexisting order parameters at low temperatures, and in addition their ME responses were generally very weak as aforementioned. To overcome the deficiency of single-phase multiferroics and to provide new approach to the magnetoelectric coupling mechanisms, recent work also concentrates on the class of artificial multiferroics in the form of composite-type materials or thin/thick film nano-/heterostructures [24, 26]. It was observed that composite-type multiferroics, which mainly include both ferroelectric and magnetic phases, yield a giant magnetoelectric (ME) coupling response even above room temperature.

The principle of ME effect in the composite system is that the magnetic-field-induced strain in the magnetostrictive component is transferred to piezoelectric component through elastic coupling, resulting in a piezo-induced voltage and vice versa. It means that in the piezomagnetic/piezoelectric composites, in presence of an applied magnetic field, piezomagnetic particles change their shape due to magnetostriction effect, and this strain is passed to the piezoelectric phase, resulting in an electric polarization change.

Thus, the magnetoelectricity in the composite system is a product property and needs biphasic surrounding to exhibit the complex behavior. The primary ME composite materials become magnetized when placed in an electric field and electrically polarized when placed in magnetic field. In the secondary effect, the permeability or permittivity change is expected [27].

The first work on ME composites was done by Van Suchtelen and other researchers at Philips Laboratories in the Netherlands [28–32]. The ME composites were prepared by unidirectional solidification of a eutectic composition of the quinary system Fe–Co–Ti–Ba–O [28, 30]. The unidirectional solidification helps in the decomposition of the eutectic liquid into alternate layers of the constituent phase: a piezoelectric perovskite phase (P) and a piezomagnetic spinel phase (S) (L $\rightarrow$ P + S). They reported to have obtained a ME voltage coefficient dE/dH = 130 mV/cmOe which is 1-2 order higher than single-phase materials, from a eutectic composition of $BaTiO_3$–$CoFe_2O_4$ by unidirectional solidification [28, 32]. The microstructure of the first ME composite is depicted in Figure 1 [28]. In 1978, Van den Boomgaard and Born [29] outlined the conceptual points inherent to the ME effect in composites. These can be summarized as (i) two individual phases should be in equilibrium, (ii) mismatching between grains should not be present, (iii) magnitude of the magnetostriction coefficient of piezomagnetic or magnetostrictive phase and magnitude of the piezoelectric coefficient of the piezoelectric phase must be greater, (iv) accumulated charge must not leak through the piezomagnetic or magnetostrictive phase, and (v) deterministic strategy for poling of the composites.

Due to the great potential for device applications, such as actuators, switches, magnetic field sensors, or new types of electronic memory devices, film type ME composites have received the significant research interests during recent years [33, 34]. Also, many bulk ME composites have been found to exhibit such a strain-mediated ME effect above room temperature [35–40]. Multiferroic ME films, in comparison with bulk ME composites, have some unique advantages. For example, ferroelectric/piezoelectric and magnetostrictive phases could be tuned and controlled at the nanoscale, representing a new scale for exploring ME coupling mechanisms. Furthermore, while two constituent phases in bulk ME composites are usually combined by cosintering or adhesive bonding, which inevitably results in loss at the interface,

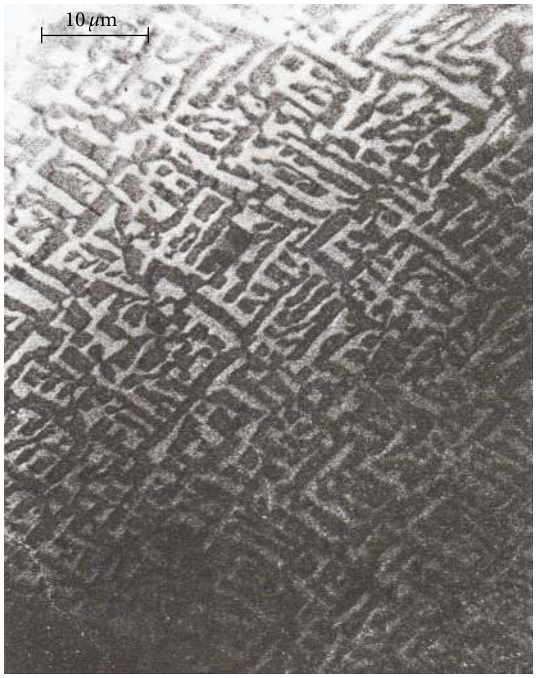


Figure 1: Microstructure of 1st ME composite by Suchtelen. Samples were fabricated by unidirectional solidification of a eutectic composition of the quinary system Fe–Co–Ti–Ba–O, [28].

in composite ME films; however, the different phases can be combined at the atomic level, and thus interface losses could be reduced significantly [2]. Therefore, multiferroic ME films are more promising candidates for use in integrated magnetic/electric devices, such as sensors, microelectromechanical systems, high-density memories, spintronics, and hybrid magnetic/mechanical energy harvesters. The renaissance of multiferroic ME films has recently been accelerated by advances in thin-film growth techniques, such as the pioneering work of Zheng et al. [34], supported by improved theoretical calculations [41–43]. In last five years, an enormous research work was carried out on ME composites materials and reviewed in various articles [2, 3, 23, 24, 44–48] because of their potential feasibilities. The detailed historical research activity done so far by various researchers among the world on ME effect of single phase, bulk composites, thin films, ME laminate composite materials as well as the theoretical simulation (Green's function, equivalent circuit approach, finite element method), ME resonance effect, ME voltage gain effect, ME gyration effect, and various applications of magnetoelectric materials (Tunable devices, gradiometer, phase shifter, magnetic field sensor, etc.) is shown in Table 1.

Nowadays, many researchers are getting attracted towards the investigations of magnetoelectric phenomenon in ME multiferroics composites due to their cross-coupling effect which lead them to be useful for many potential applications on device level. Existing literature survey reveals that there is an abundant research work that is going on the magnetoelectric interaction of various kinds of ME multiferroics composites in bulk as well as thick/thin films forms with different kinds of connectivity's schemes. The following data recorded from SCOPUS (http://www.scopus.com/) shown in Figures 2 and 3 represent the year wise number of articles published in the literature on the ME effect of bulk and thin films composite structures, respectively. Thus, it seems that there is an increasing scientific interest in magnetoelectric phenomenon which is evidenced by the rising number of publications in the last 10 years. Therefore, there is no doubt that the ME effects in multiferroics and related materials offer fascinating new perspectives from the point of view of basic research and clearly highlight the revival of interest in this phenomenon. In Table 2, we summarized some of remarkable work done so far on ME composite materials, laminates and films [49–72].

3. ME Composite Thin/Thick Films

Multiferroic ME composite thin/thick films can generally be divided into three types in a microstructural view point: (i) a 0-3 structure, which is generally a magnetoelastic material embedded in a piezoelectric matrix, (ii) a 2-2 structure, which is generally multilayer thin films of magnetostrictive and piezoelectric materials, and (iii) a 1-3 structure, such as monolayer self-assembled nanostructures as shown in Figure 4 [2].

Few works were reported on the 0-3-type nanostructure [74, 76]. Wan et al. [74] prepared a PZT-CFO composite thin film using a sol-gel process and spin-coating technique. The films exhibited both good magnetic and ferroelectric properties, and the ME effect of these films was found to be strongly dependent on the magnetic bias and magnetic field frequency. In magnetoelectric composites, usually magnetic materials have low resistivity, and ferroelectric materials have

Table 1: Historical development of ME effect.

Year	Researcher	Research activity done
1888	Rontgen	Moving dielectrics becomes magnetized in an electric field
1894	Curie	Intrinsic ME behaviour of crystal on the basis of symmetry consideration
1905	Wilson	Polarization of a moving dielectric in a magnetic field
1922	Perrier	Experimental demonstration on static ME effect
1926	Debye	Coined term "Magnetoelectric"
1959	Dzyaloshinskii	First to show violation of time-reversal symmetry in Cr_2O_3
1960	Landau	Realized that the ME response is only allowed in time-symmetric media.
1961	Astrov	Experimental confirmation of electric field induced magnetization in Cr_2O_3
1961	Rado & Folen	Expt. confirmation of magnetic field induced polarization in Cr_2O_3
1972	Suchtelen	Introduced idea of product property
1978	Boomgaard	Conceptual points for preparation of ME composites
1973	Freeman	1st conference on ME materials
1994	M. I. Bichurin	Composite magnetoelectrics: their microwave properties
1997	M. I. Bichurin	Magnetoelectric microwave phase shifters
2001	J. Ryu	1st 2-2-structured metal-ceramics laminate ME composite
2001	C. W. Nan	Theoretical calculations of the magnetoelectric properties based on the Green's function technique
2002	M. I. Bichurin	Magnetoelectric sensor of magnetic field
2003	M. I. Bichurin	1st report on the enhanced ME effects at resonance
2003	S. Dong	1st theoretical analysis of ME coefficient with an equivalent-circuit approach
2003	C. W. Nan	Numerical modeling of magnetoelectric effect in a composite structure
2004	C. W. Nan	1st report on the calculation of giant ME by using the finite element method
2004	S. Dong	1st report on high magnetoelectric voltage gain effect
2004	S. Dong	1st reported voltage gain effect in a ring-type magnetoelectric laminate
2005	M. Fiebig	1st reviewed ME effect
2005	N. A. Spaldin	The renaissance of magnetoelectric multiferroics
2005	S. Dong	1st report on high magnetic field sensitivity
2006	S. Dong	Magnetoelectric gyration effect
2006	G. Srinivasan	Ferrite-piezoelectric ME composite microwave resonator
2006	G. Srinivasan	Ferrite-piezoelectric ME composite tunable devices
2006	J. F. Scott	1st review on multiferroic and magnetoelectric materials
2007	S. Priya	Review on the development of magnetoelectric particulate and laminate composites
2007	R. Ramesh	Multiferroics: progress and prospects in ME thin films
2008	C. W. Nan	1st historical and future direction-based review on ME composites and its applications
2008	R. Grossinger	The physics of magnetoelectric composites
2008	D. Viehland	Magnetoelectric laminate composites: an overview
2009	M. Fiebig	Current trends of ME effect
2009	L. Yan	1st review article on ME effect of nanocomposite thin films
2009	J. P. Rivera	A short review of the magnetoelectric effect and related experimental techniques on single-phase (multi-) ferroics
2009	V. Bedekar	Magnetoelectric gradiometer
2010	C. W. Nan	Review article on multiferroic magnetoelectric composite nanostructures
2010	R. Ramesh	Progress report on bulk ME composites
2010	C. W. Nan	Recent Progress in Multiferroic Magnetoelectric composites: from bulk to thin films
2010	M. I. Bichurin	Present status of theoretical modeling the magnetoelectric effect in magnetostrictive-piezoelectric nanostructures
2011	F. Fang	Embedded piezoelectric/magnetic composites

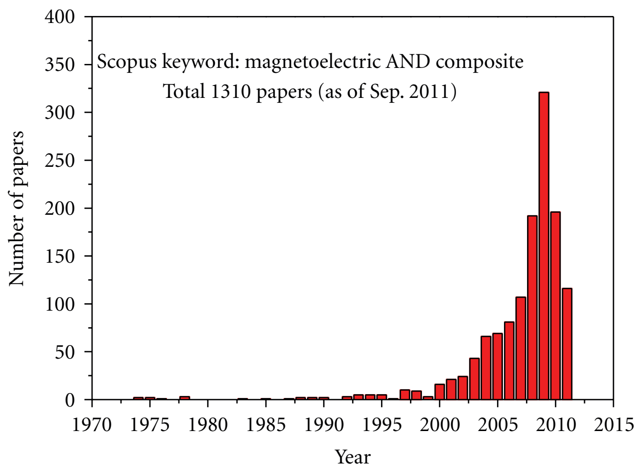


Figure 2: The year wise number of articles published in the literature on the magnetoelectric composite materials.

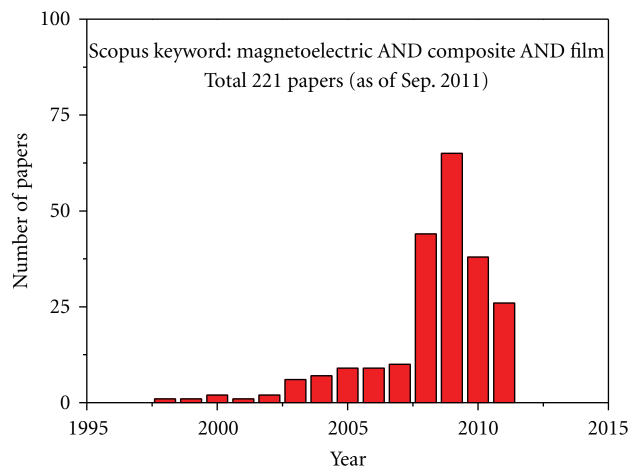


Figure 3: The year wise number of articles published in the literature on the magnetoelectric composite thin/thick films.

high resistivity [3, 24]. In particulate composite, such as above-mentioned 0-3 composite, the leakage problem due to the low resistivity in the magnetic phase is not evitable, and high electric field could not be applied to induce the polarization change in ferroelectric phase. To avoid the leakage problem, many researches are conducted on the 2-2 composites or laminate composites, where the magnetic and ferroelectric materials are stacked layer by layer. Therefore, more publications were reported on 1-3 and 2-2 heterostructures.

1-3 vertical heterostructure consists of a magnetic spinel phase epitaxially embedded into the ferroelectric matrix. The first example was reported by Zheng et al. [34], where arrays of magnetic $CoFe_2O_4$ nanopillars with diameters of 20–30 nm were embedded in a ferroelectric BTO matrix films. Other different combinations of $PbTiO_3$–$CoFe_2O_4$ and $BiFeO_3$–$CoFe_2O_4$ have also been grown on $SrTiO_3$ single crystal substrates. This kind of 1-3 composite structure is very promising because it can minimize the substrate clamping effect of each phase which is inevitable in the thin/thick films. Although these composite films showed good feasibility for ME applications, there was serious problems; no visible ME coefficient because of leakage problem resulting from low resistance of the magnetic pillars penetrating through the films or the magnetic matrix. The leakage problem would erase the promising direct ME effect in the vertical nanostructures.

As mentioned before, it has been widely accepted that ME effect is mainly caused by the strain-induced change in the interface between magnetic and ferroelectric phases, so that strong interfacial bonding between two phases are requested for a large ME response. To achieve the strong bonding, especially with the oxide materials, cofiring processing for 2-2-structured composite films was employed. However, different from the magnetic field, as electric field could be applied through only electrode with high conductivity and magnetic oxide are not enough conductive, additional metal thin film should be introduced between magnetic and ferroelectric layers. Electrically, this thin metal electrode effectively collected the generated charges from the ferroelectric and improved the piezoelectric response.

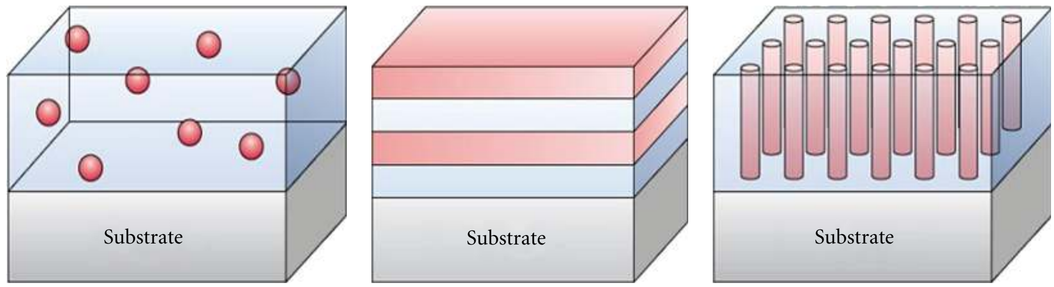
A trilayered $NiCuZnFe_2O_4$/PZT/$NiCuZnFe_2O_4$ with Ag-Pd as the internal electrode, multilayer ceramic capacitors

TABLE 2: Remarkable work on ME composite reported in the standard scientific articles.

Author/year	Composition	Connectivity	Fabrication method	Test condition (DC bias/freq.)	ME (mV/cmOe)	Remark
Van Suchtelen, Van den Boomgaard 1972,1974 [25, 28, 30, 31]	$0.62BaTiO_3$-.$0.38CoFe_2O_4$ (eutectic composition with 1.5 wt% excess TiO_2)	3-3/Unidirection solidification	Bridgman/1 atm O_2/50 cm h^{-1}	?	50	The 1st ME composite
Van den Boomgaard and Born1978 [29]	$0.60BaTiO_3$-.$0.40Ni_{0.97}Co_{0.03}Mn_{0.1}Fe_{1.90}O_4$	3-0/Particulate	Sintered at 1,300°C/24 h	500 Oe/1 kHz	80	The 1 st ME particulate composite
Suryanarayana, 1994 [49]	$0.3CuFe_2O_4$-.$0.7PbZr_{0.53}Ti_{0.47}O_3$	3-0/Particulate	Sintered at 950°C/2 h	460 Oe/100 kHz	421	The 1st resonance type ME composite
Bichurin and Petrov 1994 [50]	90% of yttrium-iron garnet and 10% PZT ceramics	3-0/Particulate	Standard ceramic method	—	—	The 1st time interaction between ME phases is discussed by striction model.
Bichurin et al. 1997 [51]	(Ni-Co)-ferrite/PZT ceramics and YIG/$BaTiO_3$	3-0/Particulate	Standard ceramic method	0.8–0.9 kOe at RT	110	The 1st theoretical approach on the magnetoelectric effect
Srinivasan et al. 2004 [52]	$Ni_{0.8}Zn_{0.2}Fe_2O_4$-0.41 vol% PZT	3-0/Particulate	Hot pressed at 1,000°C/7 Mpa	250 Oe/100 Hz	45	The 1st hot pressing method
Srinivasan et al. 2004 [52]	$Ni_{0.8}Zn_{0.2}Fe_2O_4$-0.75 vol% PZT	3-0/Particulate	Hot pressed at 1,000°C/7 Mpa	>1,000 Oe/270 kHz	3300	ME property optimization by resonance
Muzumder and Bhattacharyya 2004 [53]	BaO–TiO_2–CoO–FeO solution	3-0/Particulate	Sintered in @ 1,000–1,200°C/3 h	30 Oe/1,070 Hz	5.58	Homogeneous dispersion
Fuentes et al. 2006 [54]	$Bi_8Fe_4Ti_3O_4$	Single phase	Sintering	4,500 (f=?)	0.35	Highest ME properties from single phase material
Ryu et al. 2001, 2002 [27, 55]	PZT -20 wt%$NiCo_{0.02}Cu_{0.02}Mn_{0.1}Fe_{1.8}O_4$	3-0/Particulate	Sintered at 1,250°C	1,250 Oe/1 kHz	115	ME effect optimization from particulates composites
Kambale et al. 2009, 2010 [56, 57]	$BaZr_{0.08}Ti_{0.92}O_3/NiFe_{1.9}Mn_{0.1}O_4$ and $BaZr_{0.08}Ti_{0.92}O_3/Co_{1.2}$-$yMn_yFe_{1.8}O_4$	3-0/Particulate	Solid-state reaction sintered at 1250°C for 10 h with heating rate 5°C/min	4 kOe/50 Hz	2.34	Low ME response in bulk composites
B.K.Chougule and S.S. Chougule, 2008 [58]	$Ni_{0.8}Zn_{0.2}Fe_2O_4$ + PZT	3-0/Particulate	Solid-state reaction	6 kOe, 2.5 kV/cm	0.78	Low ME response in bulk composites
Mathe and Sheikh 2009 [59]	$NiFe_2O_4$+ PMN-PT	3-0/Particulate	Solid-state reaction sintered at 1250°C	Static ME measurement	10.43	Effect of different connectivity schemes on ME coefficient
Patankar etal. 2000 [60]	$0.45CuFe_{1.6}Cr_{0.4}O_4$-$0.55BaTiO_3$	3-0/Particulate	Sintered at 1,100°C/ 24 h	1,570 Oe/DC	0.0956	Low-temperature sintering
Priya and Islam 2006 [61]	$NiFe_{1.9}Mn_{0.1}O_4$-$Pb(Zr_{0.52}Ti_{0.48})O_3$	3-0/Particulate	Controlled precipitation route	1 kOe and 100 Oe	140	Annealing and aging effect were studied
Ryu et al. 2001, 2002 [55, 62]	Terfenol-D/$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$/Terfenol-D (PZT based ceramics materials)	2-2/Laminate	Epoxy-glued composites	4,000 Oe/1 kHz	5.150 (peak)	The 1st laminate ME composite with GMS metals

Table 2: Continued.

Author/year	Composition	Connectivity	Fabrication method	Test condition (DC bias/freq.)	ME (mV/cmOe)	Remark
Bichurin et al., 2003 [63]	$NiFe_2O_4$-PZT	2-2/Multilayer	11 layers of 13 μm $NiFe_2O_4$ 1 and 10 layers of 26 μm PZT	1,050 Oe/350 kHz@ resonance	1.200	The 1st ME multilayer composites
Zheng et al., 2004 [34]	0.65$BaTiO_3$-0.35$CoFe_2O_4$ (converse ME)	1-3/Vertically aligned structure.	PLD; single-crystal $SrTiO_3$ (001) substrates	—	—	The 1st ME 1-3 type ME composites
Dong et al., 2004 [64]	Terfenol-D/PMN-PT	2-2/Laminate	L-L laminates	$550 < H_{dc} < 800$ Oe. $f = 1$ kHz	430	L-L laminates with high ME coefficient
Wan et al., 2005 [74]	$CoFe_2O_4$-PZT	0-3/Nanostructure	Sol-gel process and spin-coating technique	1 kHz/6 kOe (10 Oe ac)	220	Successful preparation of ME composite thin films
Dong et al., 2006 [81]	FeBSiC/piezofiber laminates (Metglas/PZT)	2-1/Laminate	Epoxy-glued composites	L-L mode @ 5 Oe dc bias and $f = 1$ Hz	22000	Highest reported ME coefficient
Zhai et al., 2006 [65]	Metglas/PVDF	Layered laminate	Epoxy-glued composites	$H_{ac} = 1$ Oe and $f = 1$ kHz	7200 and 238 V/cmOe @ resonance 50 kHz	Thin and flexible ME composites
Dong et al., 2007 [66]	FeBSiC/PZNPT-fiber laminate	Layered laminate	Epoxy-glued composites	$H_{ac} = 1$ Oe.	10500@ low frequency with low dc bias 2 Oe	Long-type FeBSiC/ PZNPT-fiber laminates
Park et al., 2010 [67]	Metglas/Terfenol-D/ PMN-PZT/Terfenol-D/Metglas	Five layer laminates	Epoxy-glued composites	L-T mode $H_{ac} = 1$ Oe $f = 1$ kHz	1800	Successfully investigated the ME effect in five layered laminates
Gao et al., 2010 [68]	Metgla + PMN-PT and PZN-PT single crystals	Laminated composites	Epoxy-glued composites	$H_{ac} = 1$ Oe $f = 1$ kHz	8500	2.8 times enhanced ME coefficient is observed
Chashin et al., 2011 [69]	Metglas/PMN-PT	Laminate composites	Epoxy-glued composites	$H_{ac} = 1$ Oe $f = 1$ kHz	45000	Highest reported ME coefficient
Chen et al., 2008 [70]	Ni/PZT/Ni	2-2/Laminate	Electrodeposition	150 kHz/1.2 kOe	530	Magnetoelectric disk resonators
Park et al., 2009 [75]	PZT-PZN and $(Ni_{0.6}Cu_{0.2}Zn_{0.2})Fe_2O_4$ [NCZF]	3-2/Nanocomposite thick films	Aerosol-deposition	$H_{ac} = 1$ Oe $f = 1$ kHz	150	First 3-2 ME composite structure by AD
Xu et al., 2010 [71]	CoFe2O4/Pb(Zr0.53Ti0.47)O3	3-0 Nanocomposite thick films	Sol-gel-processing and spin-coating technique	10 kOe/50 Hz	0.4	Low magnetoelectric response
Ryu et al., 2011 [72]	$CoFe_2O_4/Pb(Zr_{0.53}Ti_{0.47})O_3$	2-2 Nanocomposite thin films	Sol-gel process and spin-coating technique	50 kHz/dynamic	273	Optimal annealing processes for ME composite thin films have been achieved.
Wan et al., 2011 [74]	PZT-PMnN + $NiZnFe_2O_4$	3-0 Nanocomposite thick films	Aerosol deposition	$H_{ac} = 1$ Oe $f = 1$ kHz	68	First 3-0 type ME composite structure by AD



(a) (b) (c)

Figure 4: Schematic illustration of three ME composite films with the three common connectivity schemes: (a) 0-3 particulate composite, (b) 2-2 laminate composite, and (c) 1-3 fiber/rod composite films, [2].

Table 3: Summary of advantages/disadvantages of ME composite films with different connectivity.

Connectivity	Advantage	Disadvantage	Remarks
0-3	Easy processing.	Low resistivity (difficult to pole). Low ME property.	Sintering with ceramic power mixture. Ceramic/polymer composite.
2-2	Easy fabrication. High resistivity. Good ME property.	Interdiffusion. Thermal expansion mismatch.	Cofiring at high temperature. All ceramic materials. Tape casting.
	High resistivity. Low-temperature processing. Coherent interface. Precise control of the lattice mismatching and thickness in the atomic scale.	Weak ME effect.	Thin film process layer by layer. Integrated ME devices.
	Easy fabrication. High resistivity.	Only bulk material. Low mechanical strength from epoxy bonding.	Epoxy bonding at room temperature. Ceramic/magnetic metal alloy.
1-3	Coherent interface in an atomic scale.	Low resistivity. Hard to fabricate.	Large in-plane strain. Thin film process.

(MLCCs) consisting of ferroelectric BT thin layers with ferromagnetic Ni internal electrodes, and PZT/$NiFe_2O_4$ laminated composites prepared by tape casting method are good examples for cofired composites [77–79]. However, occasionally high-temperature cofiring processing triggered the interdiffusion between magnetic and ferroelectric materials and deteriorated coupling in the interface. Furthermore, the thermal expansion mismatch between two materials induced the defects, such as microcrack or pores, during the cooling process, and high ME coupling could not be achieved from cofired composites with easiness.

Instead of oxide magnetic materials, metal alloy-based magnetostrictive materials, such as Terfenol-D, Ni(Mn-Ga), Metglas, and Permendur, were employed for laminar composites [80, 81]. As the metal alloy-based magnetostrictive materials could not stand at the high processing temperature for ferroelectric materials, magnetostrictive metal alloy and ferroelectric ceramic were bonded with strong epoxy at the room temperature instead of co-firing. Even though strong magnetostrictive materials were employed, ME properties did not increase as predicted. As the epoxy layer is much softer than magnetostrictive metal alloy and ferroelectric ceramic, even thin epoxy layer could absorb the generated strain and could not transfer the strain effectively between two phases.

To avoid the high-temperature reaction and diminish the thermal expansion mismatch problem from the cofiring processing, thin film deposition methods with low annealing temperature have been widely employed. Including the 2-2 type layer heterostructure films, 0-3 type particular films, and 1-3 type vertical heterostructure films were also prepared using the physical deposition methods, such as pulsed laser deposition, molecular beam epitaxial, and sputtering, and chemical processing, such as spin coating, metal-organic chemical vapor deposition [3, 24, 73, 82–84]. The 2-2-type horizontal heterostructures exhibit weak ME effects compared to the 1-3 vertical nanostru8tured films because of large in-plane constraint from substrates. However, the 2-2-type films are easy to fabricate and eliminate the leakage problem of magnetic phase. Therefore, there are several reports which showed visible ME characteristics of 2-2-type horizontal heterostructured films [85]. These ME composite thin films are more unique than bulk ME in terms of coherent interface and precise control of the lattice mismatching and thickness in the atomic scale [2, 3]. Furthermore, ME composite thin films are more attractive than bulk ME for integrated ME device applications, such as sensors, MEMS-based devices, next generation memories, and spintronics. The advantages/disadvantages of ME composite films with different connectivity are summarized in Table 3.

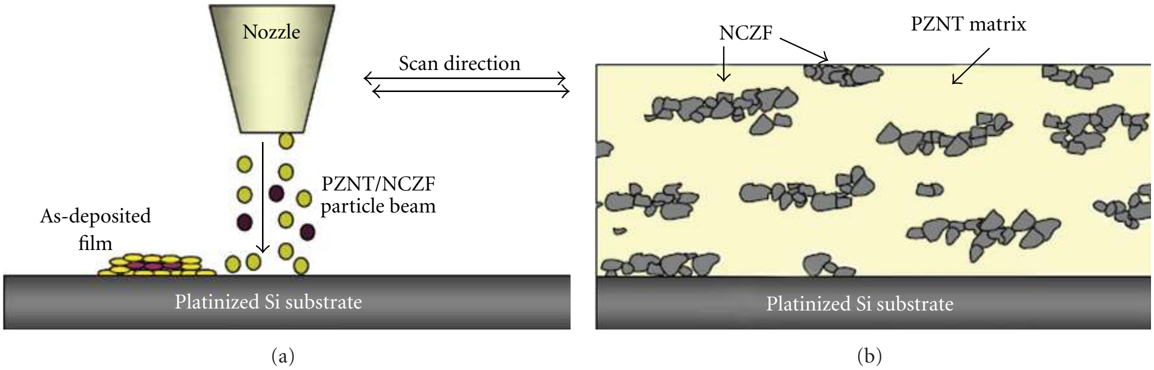


Figure 5: Schematic illustration of (a) ME composite film fabrication and (b) microstructure of nanocomposite ME films by AD, [75].

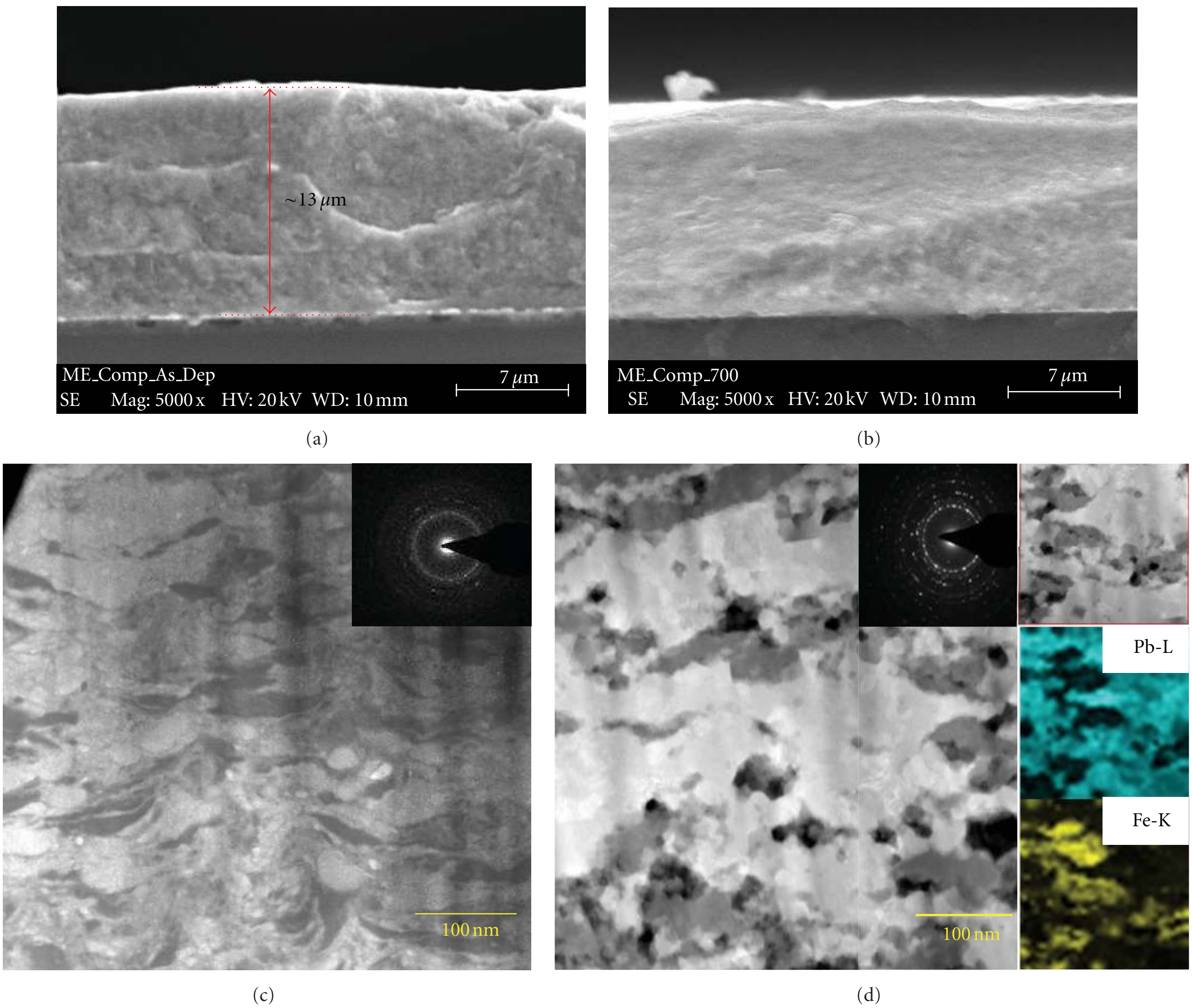


Figure 6: Microstructural analysis of 3-2 nanocomposite thick films by AD cross-sectional SEM image of (a) as-deposited and (b) annealed film. STEM micrographs and SAED of (c) as-deposited and (d) annealed film and EDX mapping.

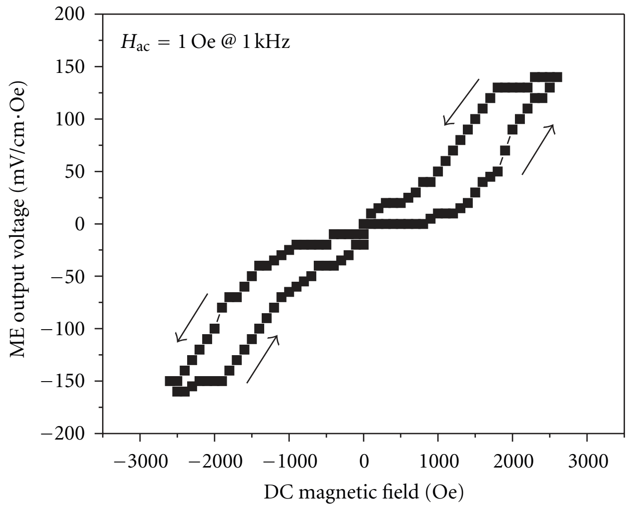


FIGURE 7: ME coefficient of 3-2 nanocomposite ME thick films by AD as a function of magnetic DC bias. The maximum ME coefficient was measured to be 150 mV/cmOe. This magnitude is about 3 times higher than the previously reported nanocomposite films by other thin film processes, [75].

4. ME Thick Films by Aerosol Deposition

In using ME composite films for real practical applications including sensors and energy harvesters, most nanocomposite/heterostructured films were limited in their thickness in terms of ME properties and processing. As the thin film had the tiny volume, its small ME signal was not easy to be detected and should have considerable thickness. For example, although some of ME composite films showed high ME voltage coefficient, the real output voltage from the samples might be miserably small (~μV level). Therefore, to obtain enough voltage signals from the ME films, the thickness should be as a several micron range at least. However, due to the difference in thermal mismatch between films and substrates as well as slow deposition rate, it is not easy to achieve the ME film with the considerable thickness. There are few reports on ME composite thick films fabrication and characterization up to date.

The Korea Institute of Materials Science (KIMS) introduced noble process technique for thick film (over 10 μm-thick) type 3-2-type and 2-2-type ME composites. They used room-temperature powder spray in vacuum process (known as aerosol deposition (AD)) to fabricate ME composite thick films. Since, AD is conducted at RT and highly dense, nanosized, crystalline ceramic films can thus be obtained with high deposition rates up to several microns/min [86, 87]. AD is a very suitable film deposition route for low sinterability, high reactive composite ceramic materials such as PZT-ferrite composite materials. Furthermore, it is very easy to control the magnetostrictive/piezoelectric phase ratio because final composition is directly reflected from initial raw powder mixture. They fabricated highly dense 3-2 nanocomposite ME thick films of PZT-PZN and $(Ni_{0.6}Cu_{0.2}Zn_{0.2})Fe_2O_4$ (NCZF) with thickness of over 10 μm on platinized silicon substrate at RT. Figure 5 shows the schematics of 3-2 nanocomposite ME films. For aerosol deposition, PZT-PZN and NCZF powders were mixed in 4 : 1 weight ratio, and the mixed powders were sprayed into an evacuated deposition chamber through nozzle. The 3-2 nanocomposite ME films were formed on a platinized silicone substrate at RT. The fabricated film thickness was controlled in the range of 10–13 μm by controlling the number of repetitions of the nozzle scan, and the microstructure was almost fully dense. Up to date, there is no report on such high-density thick ME composite films except this report. Furthermore, the fabricated nanocomposite films showed well-dispersed and laminated magnetic NCZF platelets inside of PZT-PZN piezoelectric matrix as shown in Figure 6. TEM and SAED images demonstrate that PZT-PZN piezoelectric matrix phase and NCZF inclusions were well crystallized with no trace of amorphous phase. Further, it can be seen in this STEM microstructure that the size of both PZT-PZN and NCZF crystallites was in the range of 100 nm which is enough size for piezoelectricity as well as ME property. According to the STEM image and EDX mapping, they could confirm the connectivity of synthesized composites.

This composite has ruled off the leakage problems of 1-3 nanopillar structured ME composite films and minimized substrate clamping effect, thus showed drastically improved ME coefficient over 150 mV/cmOe (Figure 7), which is higher than ever reported value from ME films.

As aforementioned, AD has an advantage on controlling the microstructures and complex connectivity, [75, 88], which are related with ME coupling. They pursued the synthesis of 3-2 ME nanocomposite films with different piezoelectric/magnetostrictive phase ratio by using the same method [72]. 0.9Pb $(Zr_{57}Ti_{43})O_3$-0.1Pb$(Mn_{1/3}Nb_{2/3})O_3$ (PZT-PMnN) and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF) were selected for piezoelectric matrix material and magnetostrictive particles, respectively. For AD, PZT-PMnN and NZF powders were mixed with various weight ratio from 15 to 30% NZF. One of the important factors for the success of AD is the particle size distribution. They used shear mixer for homogenous mixing of two particles and prevent particle size changes.

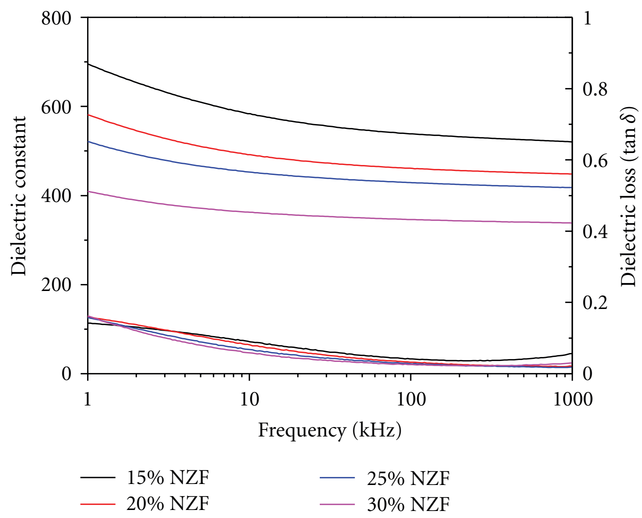


FIGURE 8: Dielectric constants and losses according to the frequency of PZT-PMnN + NZF nanocomposite films by AD as a function of NZF content, [72].

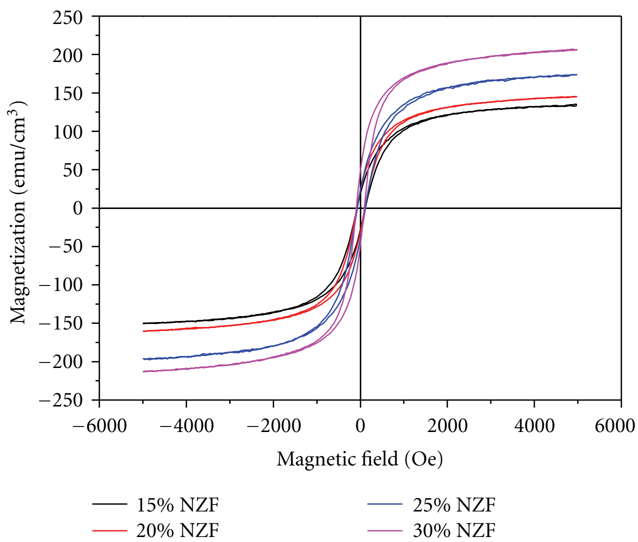


FIGURE 9: M-H hysteresis loops PZT-PMnN + NZF thick films by AD with different NZF content, [72].

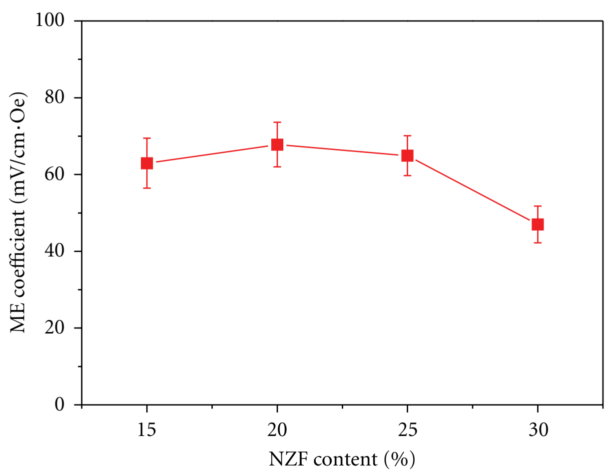


FIGURE 10: Maximum ME coefficient of PZT-PMnN + NZF nanocomposite films by AD as a function of NZF content, [72].

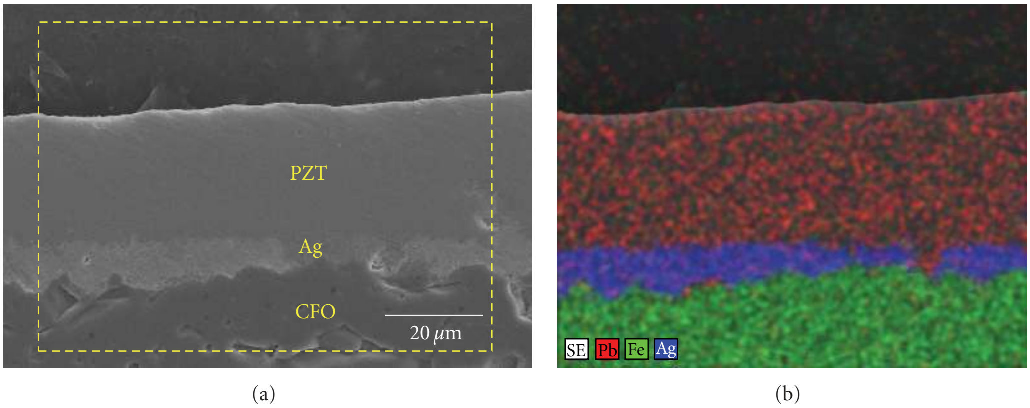


Figure 11: (a) cross-sectional SEM micrographs and (b) EDX mapping of 2-2 ME composite thick films by AD.

The composite films showed coexistence of perovskite (PZT-PMnN), and spinel (NZF) phases and peak intensities from NZF phase were changed with changing NZF content in the composite films; this means that AD can control the composition ratio of composite films by controlling raw power mixture. This is confirmed by electrical and magnetic properties as shown in Figures 8 and 9. The magnetization of composite films was measured and reflecting the ferromagnetic characteristics of all the composite films. With increasing NZF content, the remnant and saturated magnetizations were gradually increased, and coercive magnetic fields were keeping the almost the same value. This indicates that NZF content variation did not severely affect its own magnetic characteristics in the composite films. The ME coefficients were not changed severely in that NZF content range of 15∼25%, but there was drop when 30% NZF was added (Figure 10). The maximum ME output voltage was reported to be 68 mV/cmOe from 20% NZF-added composite film. This magnitude is lower than that of their previous PZT-PZN + NZCF system, but still higher than that of the nanocomposite films made by other thin film process which had maximum ME output voltages under 40 mV/cmOe [34, 83, 89]. In addition to the ME characteristics, the deposition rate of ME films was exceptionally higher (over 1 μm/min) than other conventional thin film process. By using this fabrication technique, 2-2-type laminate thick films (over 10 μm-thick) is possible as depicted in Figure 11, and the evaluation results will be published in elsewhere.

5. Conclusion

Nowadays, many researchers are getting attracted towards the investigations of magnetoelectric phenomenon in ME multiferroics composites due to their cross-coupling effect which lead them to be useful for many potential applications on device level. We presented the review on ME composite thin/thick films in this paper. A brief discussion was presented on ME multiferroics, ME composites, and ME composite films by historically and microstructurally. It seems that there is an increasing scientific interest in magnetoelectric phenomenon which is evidenced by the rising number of publications in the last 10 years. Therefore, there is no doubt that the ME effects in multiferroics and related materials offer fascinating new perspectives from the point of view of basic research and clearly highlight the revival of interest in this phenomenon. An in-depth discussion was provided on synthesis of thick ME composite films using AD. This is an extremely important development as large area deposition capability with excellent ME composite film quality which can overcome the shortcomings of other thin film processes will allow transitioning the prototype devices.

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