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Ultrahigh magnetoelectric voltage coefficients in laminates of Metglas and length-polarized ternary $0.35Pb(In_{1/2}Nb_{1/2})O_3–0.35Pb(Mg_{1/3}Nb_{2/3})O_3–0.3PbTiO_3$ single crystals

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ABSTRACT

In this paper, a magnetoelectric laminate composite based on length magnetized Metglas and length-polarized ternary $0.35Pb(In_{1/2}Nb_{1/2})O_3–0.35Pb(Mg_{1/3}Nb_{2/3})O_3–0.30PbTiO_3$ (PIMNT) single crystal has been presented. This Metglas/PIMNT L–L mode composite exhibits ultrahigh magnetoelectric voltage coefficients of ~17 V/Oe at quasi-static frequency and of ~147 V/Oe at resonance frequency, which are much larger than other magnetoelectric composites reported so far. Analysis of magnetic field sensitivity indicates that the estimated noise equivalent magnetic induction of the proposed composite is as low as 8.6 $pT/Hz^{1/2}$@1 Hz. Due to its giant magnetoelectric voltage coefficients, the maximum magnetic-field-energy-harvesting output power reaches 29.2 mW/Oe^2, which is about 3.65 times than that of previously reported Metglas/PMNT multi-push–pull mode composite. Accordingly, the proposed Metglas/PIMNT L–L mode composite shows promising applications in magnetic field detection sensors as well as transducers for magnetic field energy harvesting.

1. Introduction

In recent years, the two-phase magnetoelectric (ME) laminate composites based on magnetostrictive and piezoelectric materials have drawn significant interests due to their potential applications in many multifunctional devices, such as passive magnetic field sensors, electric-write magnetic-read memory devices, microwave filters, energy harvest devices, actuators, transducers, etc. [1–3]. Giant ME interactions can be observed in these ME laminate composites, which derive from the coupling of the magnetoelastic and elastoelectric effects of individual layers: the strain induced in one constituent (either in magnetostrictive layer or in piezoelectric layer) is transferred to the other and alters its polarization or magnetization [4].

Till now, several kinds of ME laminate composites have been experimentally and theoretically investigated: (a) ceramic composites of piezoelectric ceramic (e.g. PZT) and magnetic ferrite (e.g. CFO, NFO) [5,6]; (b) two-phase ME composites of magnetic alloy (e.g. Terfenol-D, Metglas, Fe–Ga alloy) and piezoelectric material (e.g. PZT, PMNT, PZNT) [7–10]; (c) polymer based composites of polymer matrix (e.g. PVDF, Polyurethane) and magnetic material (e.g. Metglas, Terfenol-D) [11–14]. Among them, the ME laminate composites formed by relaxor-based PMNT single crystal and Metglas possess higher ME field coefficients due to their ultrahigh piezoelectric coefficient ($d_{33,p}$ ~2000 pC/N) and piezomagnetic coefficient ($d_{33,m}$ ~4 ppm/Oe) [2]. On the other hand, the value of ME coefficient in laminate composites is determined not only by the material parameters of the constituent phases (i.e. piezoelectric and piezomagnetic coefficients, magnetic permeability, elastic constant, etc.), but also by the operation mode (i.e. orientation of the constituent phases and an applied magnetic field) [15]. Thus, ME laminate composites of various operation modes have been investigated, such as transversely magnetized and transversely polarized (T–T) mode, T-–L mode, L–T mode, and L–L mode [16–18]. In addition to these four parallel sandwiched structure, ME composite structures operating in radial mode or bending mode also receive widespread attentions [19,20].

Moreover, Dong et al. have experimentally and theoretically verified that the two-phase ME laminates in the L–L mode will have even higher ME voltage coefficient (α_V) than the T–T, T–L and L–T mode ones due to the larger electromechanical coupling factors and piezoelectric coefficients ($k_{33,p} > k_{31,p}$ and $d_{33,p} > d_{31,p}$) [4,17]. To date, the highest value of the non-resonance ME voltage coeffi-

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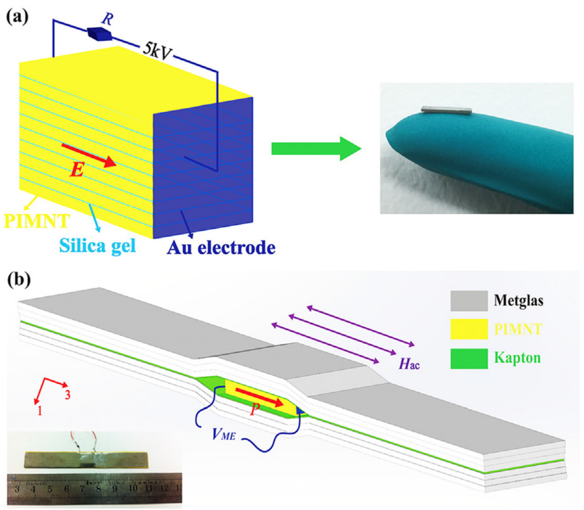

Fig. 1. (a) The schematic diagram of the stacked block and the procedures of poling the PIMNT plates. (b) The schematic diagram and photograph of the proposed Metglas/PIMNT L–L mode composite. The arrows for H_{ac} and P designate the magnetic field and electric polarization directions, respectively.

cient (α_V) is 7.79 V/Oe, which has been reported in Metglas/PMNT composite with a multi-push–pull mode [2]. It must be noted that the ME voltage coefficient (in units of V/Oe) rather than the ME field coefficient (in units of V/cm Oe) is adopted in our research. From the practical point of view, enhancing the ME voltage coefficient is an important goal, which will enable the composites to meet the application demands for sensors and transducers [21–24].

In this paper, a ME laminate composite of length-polarized ternary $0.35Pb(In_{1/2}Nb_{1/2})O_3$–$0.35Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.30PbTiO_3$ (PIMNT35/35/30) and length-magnetized Metglas has been constructed, which exhibits an ultrahigh ME voltage coefficient of ~17 V/Oe at quasi-static frequency and of ~147 V/Oe at resonance frequency. Analysis of magnetic field sensitivity indicates that the estimated noise equivalent magnetic induction (NEB) of the composite is as low as 8.6 pT/Hz$^{1/2}$@1 Hz. In addition, the maximum magnetic-field-energy-harvesting output power reaches as high as 29.2 mW/Oe^2 under an optimal 380 kΩ load resistance. Compared with previous Metglas/PMNT multi-push–pull mode composite, this Metglas/PIMNT L–L mode composite exhibits the advantages of higher ME voltage coefficient, improved output power and simple fabrication process.

2. Experimental procedure

Fig. 1(b) shows a schematic diagram and a picture of the Metglas/PIMNT L–L mode composite. A high-quality PIMNT35/35/30 single crystal was grown from the melt by a modified Bridgman technique [25] and then diced into the 001-oriented plates with dimensions of $10^{[\text{length}]} \times 5^{[\text{width}]} \times 0.5^{[\text{thickness}]}$ mm^3. Compared with binary single crystal of PMNT, the ternary single crystal of PIMNT35/35/30 exhibits much higher coercive field (E_c ~5.85 kV/cm at 20 °C) and phase transition temperatures (T_{rt} ~127 °C, T_C ~187 °C) [26], which can effectively extend the operating temperature and voltage range of the composite. However, the longitudinal poling of the PIMNT plate will be much more difficult than transverse poling because of the long electrode distance and high coercive field. So we have proposed a laminated-poling method to make sure that the PIMNT plates could be successfully poled along length direction in an efficiency way, as shown in Fig. 1(a). Firstly, ten as-prepared PIMNT plates were stacked one on top of each other along thickness direction, and bonded with thin silica gel layers to form a stacked block. After deposition of Au electrode, the stacked block was poled using an electric field of 5 kV at 160 °C for 15 min with the same voltage in the subsequent cooling process. The flexibility of the silica gel ensured that the stress in PIMNT plates was completely released during the polarization process, which was crucial for getting crack-free PIMNT layers. To ensure the comparability of the experiments, the polarized PIMNT plates were carefully selected based on the values of initial capacitance (C_P^0 ~11 pF@1 kHz), piezoelectric constant (d_{33} ~2000 pC/N) and dielectric loss (tanδ ~4‰).

The Metglas ribbons (Vacuumscheltze GmbH & Co., KG, Germany) and Kapton insulating films (DuPont Kapton HN, 25 μm of thickness) were cut into dimensions of 80 × 10 × 0.025 mm^3. West System 105/206 resin/hardener were employed as the epoxy in the laminates. The epoxy (~100 mg) was applied manually to one Metglas layer. Then the Metglas layer was mounted onto a spinner and processed at 1500 rpm for 1 min to distribute the epoxy. Three numbers of such Metglas layers were stacked one on top of each other, and attached on the bottom and top surfaces of the PIMNT layer. In order to prevent electrical discharge of the composite and eliminate the distributed capacitance, N layers of Kapton films were assembled symmetrically between the PIMNT and Metglas layers using the same process. The assembly was pressed by a vacuum-bag method and cured at 50 °C for more than 10 h under a vacuum pressure of -24 in-Hg. On the other hand, the quality and the thickness of the bonding layers in ME laminate composites play an extremely important role of getting high ME responses [27]. Here, the employed spin-coat/vacuum-bag process ensured the uniformity of interfacial epoxy layers, which could make the coupled stress induced by H_{ac} be coplanar with the poling direction of the PIMNT plate. And an optical micrograph of a cross section of the laminate indicated the epoxy layers at the Kapton/Metglas and Metglas/Metglas interfaces with a uniform thickness of ~20 μm.

In the quasi-static frequency range ($0 < f < 18$ kHz), due to the high impedance of the Metglas/PIMNT composite, the ME voltage coefficient (α_V) could be measured by a derivative method, which was determined from the ME charge coefficient (α_Q) and capacitance (C_P) of the composite (i.e., $\alpha_V = \alpha_Q / C_P$) [10,28]. With the increase of frequency, the impendence of the composite declined dramatically. Therefore, the ME voltage coefficient was measured by lock-in amplifier (Signal Recovery 7270) directly in the high frequency range of 18,020 Hz < f < 83,520 Hz. The dielectric properties and impedance characteristic of the composite were measured using an impedance analyzer (Agilent 4294A). The DC resistance (R_{dc}) was obtained based on Ohm's law using the high resistance meter (Agilent 4339B). The ME charge coefficient was measured under a constant AC magnetic drive of H_{ac} = 0.1 Oe which was generated by a custom-built Helmholtz coil and a Keithley 6221 current source. The H_{bias} was generated by an electromagnet (Litian magnetic technology Co., Ltd, China). The charge was measured by a charge amplifier (Brüel & Kjær 2635), and output of the charge amplifier was measured by a dynamic signal analyzer (Agilent 35,670A).

3. Results and discussion

The capacitance of the PIMNT plate before making ME composite, i.e. the initial capacitance (C_P^0 ~11 pF at 1 kHz), was really small and the value would fall further when the plate was clamped by the Metglas layers [29]. On the other hand, in the multilayer Metglas/PIMNT composite, the Metglas layers acted like capacitor electrodes, resulting in distributed capacitance. Similarly, distributed capacitance also occurred between the terminal electrodes and the Kapton layers, as shown in Fig. 2(a). Nevertheless, only the capacitance of PIMNT layer (C_{piezo}) in the composite was of interest to us and could make contributions to the ME charge coefficient. So