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Fabrication and magnetoelectric effect of 1–3 type composites with microscale (K,Na)NbO$_3$-based Pb-free piezoceramic pillars embedded in CoFe$_2$O$_4$-epoxy matrix

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Abstract

Microscale magnetoelectric composites with 1–3 connectivity structure were fabricated by a dice-and-fill method. Mechanically sliced microscale pillar arrays of (K,Na)NbO$_3$-based ceramics were used as the piezoelectric phase, which were embedded in a hybrid matrix composed of ferromagnetic CoFe$_2$O$_4$ particles bonded with epoxy. Commercial CoFe$_2$O$_4$ nano-powder and CoFe$_2$O$_4$ particles derived from a sol–gel method during the filling process were used in two sets of samples, respectively. Obvious ME response signals were detected to be switched with the applied magnetic field. It was deduced that the different ME coefficient values of the two composites were mainly due to the interface morphology between the piezoelectric pillars and the matrix.

Keywords: B. Composites; D. Niobates; Magnetoelectric; 1–3 connectivity

1. Introduction

Magnetoelectric (ME) composites composed of ferroelectric and ferromagnetic phases, have drawn increasing interest, because of its stronger ME effect above room temperature compared to single-phase ME materials [1,2]. The ME effect as a coupling effect between the electric and magnetic polarizations is characterized by the appearance of an electric polarization on applying a magnetic field or a magnetic polarization on applying an electric field [1,3]. So far, large ME effect has been observed in both bulk composites and composite films with various types of phase connectivity [4–7]. In the 1–3 type composite thin films, Zheng et al. [6] prepared vertical heterostructure BaTiO$_3$–CoFe$_2$O$_4$ (BTO–CFO) nano-composite thin films with CFO nano-pillars embedded in BTO matrix. A distinct magnetization drop at the ferroelectric Curie temperature was observed and thus indicated the coupled effect. In a larger scale, pseudo-1–3 type PZT/Terfenol-D-epoxy (TDE) composites were fabricated with a large ME effect of the order of 300–500 mV/(cm. Oe). [7].

Among the reported 1–3 type ME composites, lead-containing materials were most commonly used due to its excellent piezoelectricity. For environmental and safety concerns, lead-free piezoelectric materials are highly desired. (K,Na)NbO$_3$ (abbreviated as KNN)-based ceramics are one of the most promising lead-free candidates [8,9], especially Li/Ta-modified KNN (abbreviated as KNN-LT) ceramics with good piezoelectric properties [10,11]. On the other hand, to explore the size effect with a vision for promising applications of ME micro-devices, more work is required to develop the fabrication process of microscale 1–3 type ME composites. This study reports on the processing and property evaluation of 1–3 type ME composites with microscale KNN-LT ceramic pillars embedded in a ferromagnetic matrix.

2. Experimental

The KNN-LT ceramic used had a nominal composition of $(K_{0.485}Na_{0.515+0.02})_{0.914}Li_{0.086}(Nb_{0.942}Ta_{0.058})O_3$, which was optimized to possess a high piezoelectric response ($d_{33} = 225$ pC/N) by our previous study [11]. To produce square-shaped micro-pillars, a set of parallel grooves were made on the ceramic disks and backfilled with wax to support

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the freestanding slabs, and then the disks were diced along another direction perpendicular to the grooves. By using this method, arrays of KNN-LT micro-pillars with a dimension 150 μm × 150 μm × 500 μm and a spacing of 200 μm were obtained.

Cobalt ferrite ($CoFe_2O_4$, abbreviated as CFO) was selected as the ferromagnetic phase because of its good magnetostrictive characteristic. A chemical solution deposition process was proposed to backfill the micrometer-sized spacing. Solutions of $Co(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were mixed at its stoichiometric ratio in a solvent of 2-methoxyethanol (2-MOE). Then the mixed solution was repeatedly infiltrated into the spacing between the micro-pillars and pyrolyzed at 400 °C for 3 min by a rapid thermal process. Finally, the pyrolyzed specimen was annealed at 700 °C for 5 min for crystallization and then infiltrated with epoxy in a vacuum to strengthen the bonding. Meanwhile, CFO nano-powder (99%) was mixed with epoxy (about 23.6 wt% CFO in epoxy) and infiltrated into another micro-pillar array as a reference. After the epoxy hardened, surfaces of both samples were polished to the end of the ceramic pillars and painted with silver electrodes. The samples were labeled with Cke-s (from solution) and Cke-p (from powder) and poled under their respective maximum tolerance electric field of 1.2 and 2 kV/mm in silicone oil at room temperature. For comparison, KNN-LT ceramic disks before dicing were also painted with electrodes and poled.

The crystal structure was investigated by X-ray diffraction (XRD, D/max-RB, Rigaku, Tokyo, Japan) using Cu-K_α radiation. The surface morphology and the cross-sectional microstructure were observed by scanning electron microscopy (SEM, JSM6460, Tokyo, Japan). The ferroelectric and ferromagnetic hysteresis loops were measured by using a ferroelectric tester (TF 2000 analyzer, axiACCT, Aachen, Germany) and a ferromagnetic tester (PPMS-9T, Quantum Design, Inc., America), respectively. The piezoelectric constant was measured by a quasi-static piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science). To measure the ME coefficient, both electrodes of the samples were bonded with a copper wire and a small sine disturbing magnetic field H_{ac} of 1 kHz generated by a Helmholtz coil superimposed on a bias magnetic field H_{dc} was applied to the sample. The induced voltage signals were monitored by a lock-in amplifier (SR850, Stanford Research Systems, Inc., America). All measurements were performed at room temperature.

3. Results and discussion

The XRD patterns (not shown) of representative composite samples of Cke-s and Cke-p distinguished the main peaks of spinel phase (CFO crystals) from the perovskite phase (KNN-LT pillars). In addition, the various phases can be directly seen by SEM as shown in Fig. 1(a)–(d). KNN-LT pillars before being filled with CFO and epoxy are shown in Fig. 1(e) for comparison. In both samples, some brightly contrasted clusters, identified to be CFO by EDX, are distributed in the gray matrix between the ceramic pillars. The EDX line analysis of Cke-s with selected elements Nb, Co, Fe is shown in Fig. 1(f) as an example. The element distribution matches well with the insert morphology photograph. In general, both the XRD patterns and the SEM images prove the formation of 1–3 type KNN-LT/CFO-epoxy composites of Cke-s and Cke-p. The difference is that in Cke-s, CFO tended to form dendritic clusters and adhere to pillar wall while in Cke-p, CFO tended to form round clusters in epoxy matrix.

The average measured d_{33} value of Cke-s is 43 pC/N, much lower than the calculated value (128 pC/N) by the modified series and parallel model [12]. The main reason for the low value is the unsaturated polarization. As shown in Fig. 1, the CFO phase in Cke-s tends to form dendritic clusters and linked together. Thus the low resistance CFO phase nearly penetrated through the composite. Besides, the epoxy became easily flexible to the thermal effect and thus could not resist the KNN-poling temperature (120–140 °C). As a result, the poling temperature and the applied electric filed were restricted, leading to the unsaturated polarization. The thermal effect also affected sample Cke-p; as a result, its average measured d_{33} (76 pC/N) is also lower than the calculated value. However, this value is higher than Cke-s because less CFO phase penetrated through Cke-p and lower leakage current was generated. Fig. 2 shows the polarization–electric field curve of the KNN-LT bulk ceramic and the magnetization–magnetic field curves of CFO nano-powder and Cke-s to support the coexistence of ferroelectricity and ferromagnetism in the composites and thus a coupled ME effect is predicted.

The ME voltage coefficient α_E is defined by Eq. (1)

$$\alpha_E = \frac{dV}{dH \cdot t} = \frac{dE}{dH} \tag{1}$$

where V is the response voltage to the applied magnetic field H and t is the effective thickness of the piezoelectric phase. A dynamic method was used in our testing to measure the α_E, the theory of which can be found elsewhere [13]. Typical response voltage signals were observed to be switched with the applied magnetic signals. This phenomenon directly proves the ME property of the prepared composites. Additionally, α_E of both samples increases approximately linearly in the low field range but decreases at high field as shown in Fig. 3. This trend of α_E is attributed to the piezomagnetic phase, since its magnetostriction increases with the field until saturation. The saturated magnetostrictive strain is transferred to the piezoelectric phase and a constant electrical signal is generated in spite of the increasing magnetic field. As a result, the α_E decreases at high magnetic field by Eq. (1).

When the piezomagnetic phase fraction is lower than an optimized value, more piezomagnetic substance favors higher ME coefficient [2]. In this study, restricted by the fabrication process, the CFO fractions are far lower than the optimized value. Therefore, the more the CFO content, the higher α_E of the composite. However, though Cke-p has a higher CFO content than Cke-s, displayed in Fig. 1(a)–(d), the α_E of Cke-s is higher than Cke-p. This can be explained by the interface morphology between KNN-LT pillars and the CFO-epoxy matrix. In Cke-s, lots of CFO clusters adhere to KNN-LT pillars

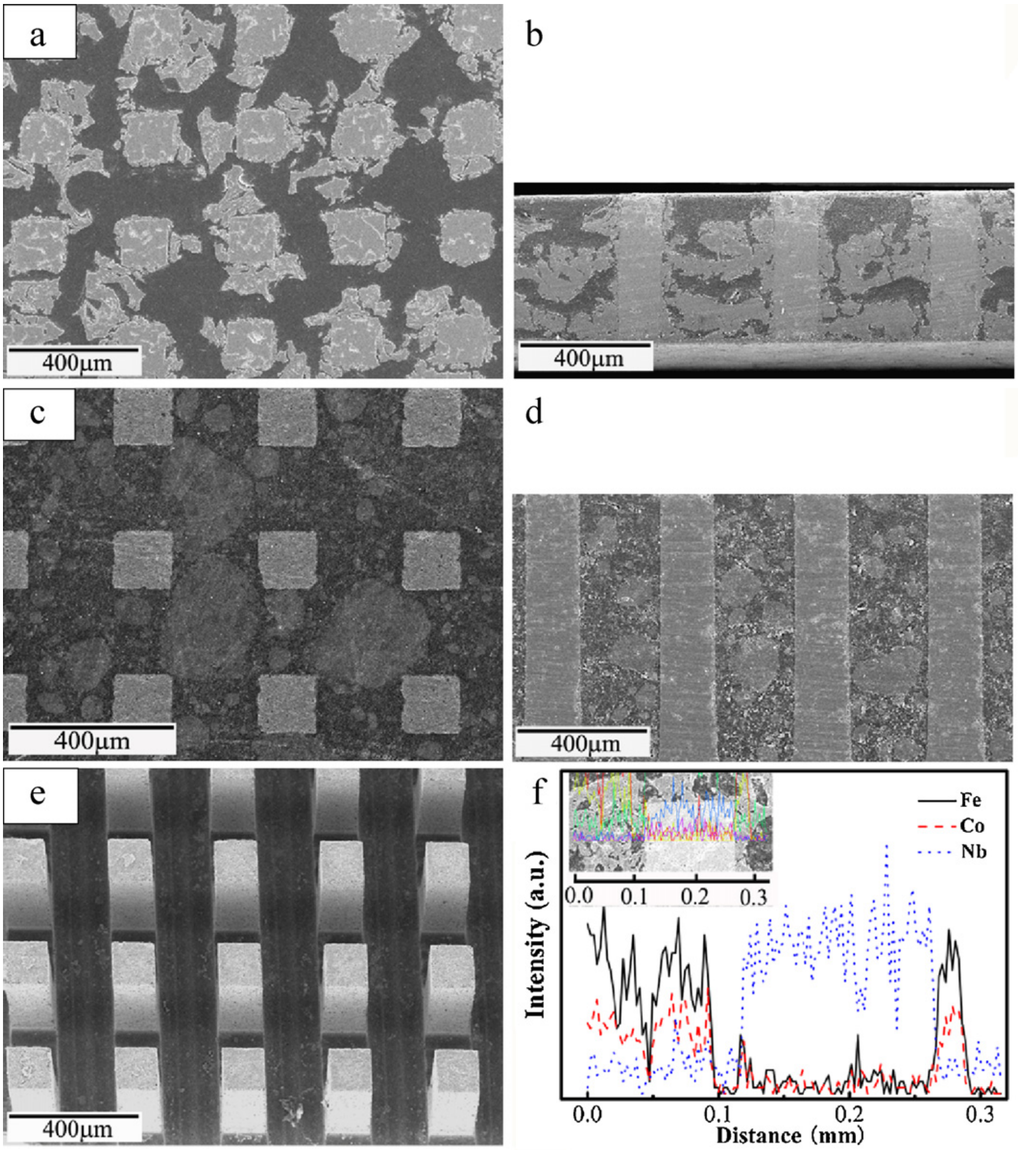

Fig. 1. Scanning electron micrographs and line-scanning results. (a, b) Surface morphology and cross-section morphology of Cke-s; (c, d) surface morphology and cross-section morphology of Cke-p; (e) KNN-LT pillar array; (d) line-scanning results of Cke-s surface.

and produce direct contacts, while CFO particles in Cke-p are packed by the epoxy matrix and indirectly contact KNN pillars, as shown in Fig. 4. The direct contacts ensure the effective strain transfer and thus Cke-s shows higher ME coefficients. Moreover, the corresponding magnetic field (H_m) to the maximum α_E value of Cke-s is much lower than that of Cke-p. This is related to the relative size of the piezomagnetic phase [14]; the CFO phase was sintered together in Cke-s while the CFO phase used in Cke-p was nano-powder with no following thermal treating.

However, the maximum ME voltage coefficient α_E of Cke-s, obtained at 1000 Oe, was about 0.6 mV/(cm·Oe), much lower than the 1–3 type PZT–TDE composites [7]. One of the main reasons lies in the far lower piezoelectric constant of Cke-s (43 pC/N) than the PZT-based composites and the lower magnetostriction constant than Terfenol-D, while the ME coefficient is directly proportional to the piezoelectric constant and the magnetostriction constant [2]. Second, the effective piezomagnetic phase is far less than optimization, while its fraction largely influences the coupling effect [2]. Third, the inactive phase epoxy also attributes to the low α_E because it absorbs parts of the strain energy when the strain generated in the piezomagnetic phase is transferred through the epoxy media to the piezoelectric phase. Accordingly, measures can be taken to improve the coupling effect. First, a pseudo 1–3 type structure can be introduced to pole the sample sufficiently without the leakage current problem. Second, CFO contents should be optimized to maximize the coupled effect. Third, high-aspect-ratio and small-scale lead-free piezoceramic pillar

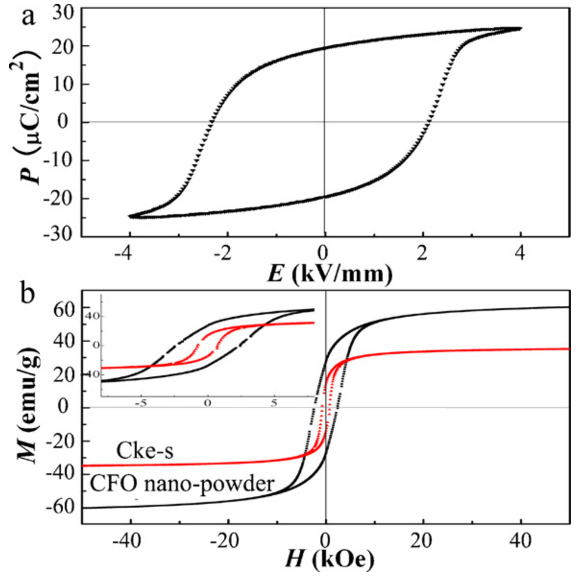

Fig. 2. Polarization and magnetization hysteresis curves. (a) *P–E* hysteresis loop of KNN-LT ceramics; (b) *M–H* hysteresis loops of Cke-s and CFO nano-powder.

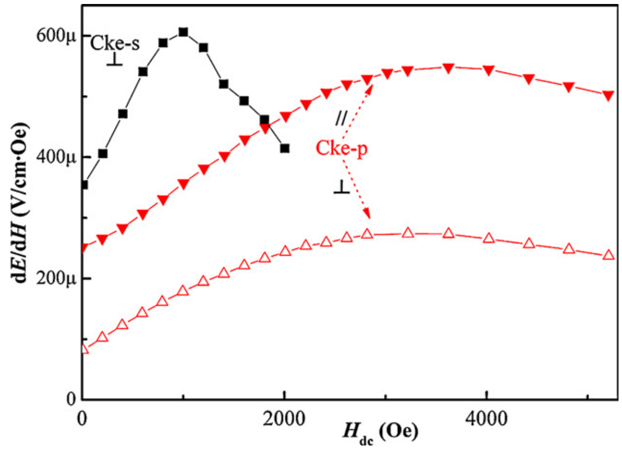

Fig. 3. The α_E values changed with the bias dc magnetic field H_{dc} at 1 kHz; perpendicular (⊥) and parallel (//) to the rod standing direction.

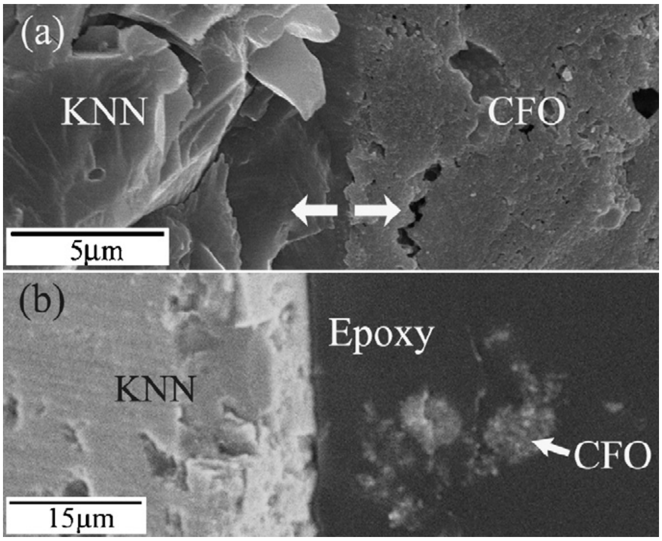

Fig. 4. The interfaces between KNN-LT pillars and CFO-epoxy matrix. (a) Cke-s; (b) Cke-p.

arrays can be introduced, which favors the thickness mode and matches the requirements of special micro-device.

4. Conclusions

One-three type KNN-LT/CFO-epoxy magnetoelectric composites were fabricated by a modified dice-and-fill method with pillars of dimension 150 μm × 150 μm × 500 μm and spacing 200 μm embedded in a CFO-epoxy matrix. The phase structure, micro-morphology, ferroelectric testing and ferromagnetic testing proved the component phases of the composite and predicted a coupled ferroic behavior. This prediction was directly proved by the voltage signals induced by applying a magnetic field. The maximum ME voltage coefficient α_E was about 0.6 mV/(cm. Oe) obtained at 1000 Oe at 1 kHz. Further study needs to be carried out to enhance the ME coefficient. However, it suggests an alternative method of fabricating 1–3 type multiferroic composites with embedded micro-scale pillars.

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