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Mn and Sm doped lead titanate ceramic fibers and fiber/epoxy 13 composites

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Manganese and samarium doped lead titanate [$\text{Pb}_{0.85}\text{Sm}_{0.10}(\text{Ti}_{0.98}\text{Mn}_{0.02})\text{O}_3$, PSmT] fibers were prepared by sol-gel method. The micrographs obtained using scanning electron microscope show that PSmT ceramic fibers are round and dense. The diameter of the fibers was in the range of 30–35 μm . The crystalline grains size is $\sim 2.5 \mu\text{m}$. The micrographs obtained using transmission electron microscope also unveiled the layer-by-layer 90° domains in the grains. X-ray diffraction patterns of the fibers show that PSmT ceramics have a pure perovskite structure. The c/a ratio of the unit cell was 1.04. The PSmT fiber/epoxy 1-3 composites were fabricated by filling the ceramic fiber bundle with epoxy. The dielectric permittivity ϵ , electromechanical coefficient k_t , and the piezoelectric constant d_{33} of PSmT fiber/epoxy 1-3 composites with 68% fiber loading were 118, 0.51, and 48 pC/N, respectively. The hysteresis loop of the composites was measured by the Sawyer–Tower method. It was also found that the composites could withstand an electric field of 15 kV/mm at room temperature. © 2004 American Institute of Physics. [DOI: 10.1063/1.1711160]

I. INTRODUCTION

Samarium and manganese doped lead titanate [$\text{Pb}_{0.85}\text{Sm}_{0.10}(\text{Ti}_{0.98}\text{Mn}_{0.02})\text{O}_3$, PST] ceramics have large piezoelectric anisotropic properties. Their k_t/k_p ratio is up to ~ 10 .^{1–3} Using this ceramics as resonators can reduce the coupling between the thickness and lateral resonances to minimize the energy loss. For an ultrasonic resonator, the frequency constant N_t is the product of thickness multiplied by the resonance frequency. So, the thickness of a high frequency resonator is usually very thin. But the electrical impedance of the resonator decreased when its thickness decreased. According to the equivalent circuit of a piezoelectric resonator, the electric impedance Z is related to the radiation resistance R_1 , free capacitance C_0 , motional capacitance C_1 , and inductance L_1 of the resonator by

$$\frac{1}{Z} = j\omega C_0 + \frac{1}{R_1 + j(\omega L_1 - 1/\omega C_1)}. \quad (1)$$

Due to its high relative permittivity (1500–4000), the electric impedance of a PZT resonator (with diameter of 5 mm and resonance frequency >15 MHz) will be reduced to only a few ohms. This value causes a great mismatch to the normal 50 Ω standard electrical coupling. Samarium and manganese doped lead titanate ceramics have a low dielectric permittivity ($\epsilon_r \sim 180$ –200). The capacitance C_0 ($C_0 = \epsilon_0 \epsilon_r \text{ area/thickness}$) and C_1 of a PSmT ceramic resonator

are much lower than that made from PZT ceramics. So this ceramics has a good potential for high-frequency ultrasonic transducer applications. Combining PSmT with epoxy to form 1-3 composites can further improve the piezoelectric anisotropy and also can decrease the relative permittivity. These properties are very useful for high frequency transducer applications.

Since other researchers have studied this ceramic, most of the present work was focused on the piezoelectric property improvement.^{4,5} The hysteresis characteristics of PSmT ceramics have received little attention thus far and as far as we know, the hysteresis loops of PSmT have not been reported in the literature. It may be because: (1) the coercive field of this ceramics is high, which implies that domain switching in PSmT ceramic is relatively difficult. (2) It is difficult to fabricate dense ceramics which could withstand high electric field (especially withstand more than 10 kV/mm).

This paper reports on dense PSmT ceramic fibers and PSmT fiber/epoxy 1-3 composites, which can withstand an electric field of up to 15 kV/mm. Based on this outstanding electrical strength, we managed to measure the hysteresis loop of the PSmT/epoxy composites.

II. EXPERIMENTS

A. Preparation of PSmT ceramic fibers

According to the formula $\text{Pb}_{0.85}\text{Sm}_{0.10}(\text{Ti}_{0.98}\text{Mn}_{0.02})\text{O}_3$, lead acetate (with 2% excess), samarium acetate, and manganese acetate were weighed up and heated at 135 $^\circ\text{C}$ for 8 h

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to remove the water of hydration. The dry salts and titanium butoxide were dissolved in methoxyethanol. After refluxing for 30 min, a brown solution was obtained. The solution was filtered and hydrolyzed with a mixture of water, methoxyethanol, and propionic acid ($\text{H}_2\text{O}:\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}:\text{CH}_3\text{CH}_2\text{COOH}=1:5:3$ in mole ratio). The amount of water could affect the viscosity of the solution and the gel fiber quality. If there were not enough water, the gel fiber would adhere to each other. If the water was too much, it is easy to form precipitate or solid gel. So the $\text{Ti}:\text{H}_2\text{O}$ mole ratio was controlled within 0.5–0.7:1. The hydrolyzed solution was concentrated until it becomes honey-like. Then it was poured into a metal container of a fiber-spinning machine (Model OneShot III, Alex James & Assoc., Inc.). The gel fibers were spun out through a spinneret, which has a pinhole of 100 μm diameter. Because the viscosity of the sol increases with the temperature decreasing, the fibers were drawn at 75 °C and wound with velocities ranging from 20 to 100 m/min. By adjusting the drawing speed, the fibers with diameter of 25–50 μm can be fabricated. The fabrication processes are same as the fabrication of PZN-PZT [zinc and niobium modified lead zirconate titanate, $0.30\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.70\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$] ceramic fibers.⁶ The fresh gel fibers are yellow. Their color will change into brown gradually in the open air. This is mainly due to the oxidation of the manganese ions.

The fiber bundles were placed on top of a ceramic powder layer that has the same composition as the ceramic fibers. Then they were hydrolyzed in moisture for one week and dried at 60–80 °C for several hours. A spoonful of carbon black was scattered around the fiber bundle for reducing the oxygen pressure in the crucible at high temperature. The fibers were covered with a crucible and heated to 280, 410, and 550 °C, respectively, at a rate of 1.5 °C/min. The fibers were heated for 1 h at each temperature step. The furnace was cooled down and the remaining carbon black was removed. Then the fibers were heated to 850 °C at a rate of 3.5 °C/min and kept at that temperature for 2 h. The temperature was increased to 1150 °C using the same heating rate and kept at that temperature for 1.5 h. Finally, the fibers were cooled down naturally. The resulting ceramic fibers were black. The diameter of the ceramic fibers was about 35 μm .

B. Fabrication of PSmT ceramic fiber/epoxy 1-3 composites

A fiber bundle was insert into a polymer tube that was sealed on one end and filled with epoxy (Epoxy 618, hardener: Polyamonoester T31). After degassing for 30 min and heated at 80 °C for 12 h, a PSmT ceramic fiber/epoxy 1-3 composite rod was obtained. The rod was sliced into disks with thickness of 200 μm . These composite disks were ground to proper thickness, polished, and deposited with chromium/gold electrodes on both sides. The hysteresis loop of the composites was measured by the Sawyer–Tower method. After poling, the piezoelectric properties were measured by an impedance analyzer HP4294A and a d_{33} meter.

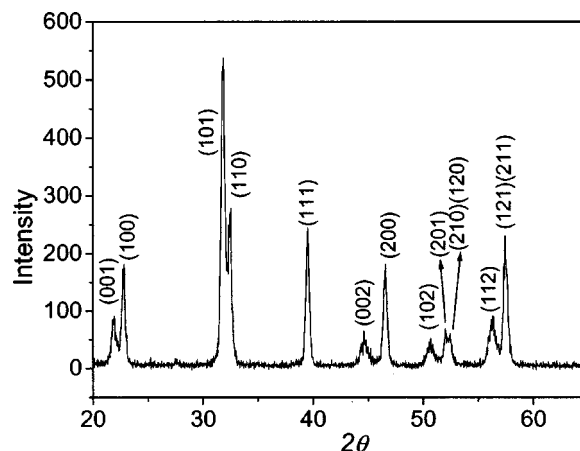


FIG. 1. X-ray diffraction patterns of the PSmT ceramic fiber.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of the ceramic fiber powder. The fibers have a tetragonal structure. According to the data of the peaks, the parameters of the crystal cell were calculated. They are $a=3.899 \text{ \AA}$, $c=4.054 \text{ \AA}$.

Figure 2 shows the scanning electron microscope (SEM) micrograph of a PSmT ceramic fiber. The fiber was dense and round. The diameter of the fiber was about 35 μm . The crystal grain size on the fiber cross section was 2–3 μm . It was found that lead excess affects the morphology of the fiber cross section. Figure 3 shows a SEM micrograph of a PSmT ceramic fiber with lead excess of 6%. Sintering conditions of this fiber are the same as that of the fiber shown in Fig. 2. It is seen that the grain boundary was not as clear as that shown in Fig. 2. Enlarged SEM micrograph (seen in Fig. 4) shows that the crystal grains were also broken. The terraced morphology is the domain layer structure. It is mainly due to the excess lead oxide can form liquid phase. The liquid phase can improve the crystal grain growing and self-consummate. Furthermore, this liquid makes the glass material easy to diffuse from grain boundary and the grain boundary became thinner. Subsequently, the interaction between the grains was stronger. When the fiber was broken to expose

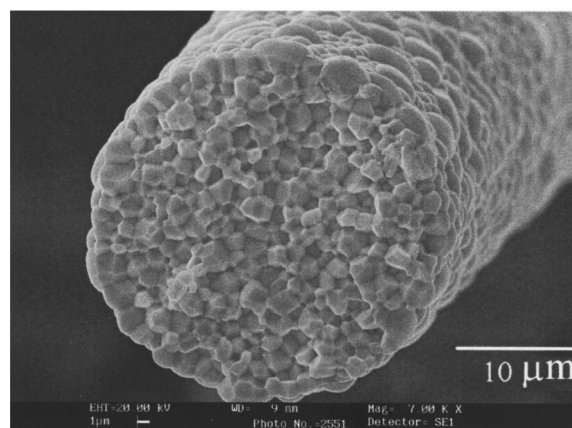


FIG. 2. SEM micrograph of a PSmT ceramic fiber with 2% lead excess.

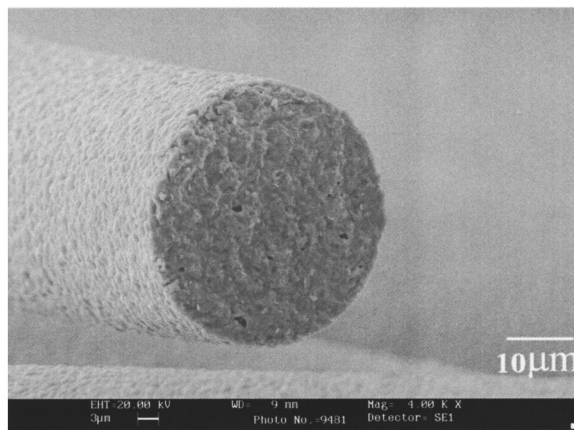


FIG. 3. SEM micrographs of a PSmT ceramic fiber with 6% lead excess.

the cross section, the section may break through the grains. On the other hand, the liquid material filled in the gap between the crystal grains and blocked the gas from evolving in the fiber. Some pores were formed. As shown in Fig. 4, the size of the pores was much smaller than that in ceramics made from mixing oxides.

Figures 5(a) and 5(b) show the micrographs of the PSmT ceramic fiber, which was obtained using a transmission electron microscope (TEM). It is seen that PSmT ceramics has 90° domains with a layer structure. The layer thickness is ~ 100 nm. The end of the domains was like “wedges” as shown in Fig. 5(b). Figure 6 shows the electron diffraction patterns of the PSmT ceramic fibers. The patterns reveal that PSmT ceramic fibers have a tetragonal structure. This result agrees with that of x-ray diffraction.

Figure 7 shows the SEM micrograph of a PSmT fiber/epoxy 1-3 composite. It can be seen that the fibers with diameter of $30\text{--}35\ \mu\text{m}$ are well packed. The ceramic fiber volume fraction is ~ 0.68 , which was measured by area integration.

Figure 8 shows the hysteresis loop of the PSmT/epoxy 1-3 composite under a 5 Hz frequency alternating current at room temperature. It is seen that the patterns under low electric fields are like curves for capacitors. When the electric field was up to $10\ \text{kV/mm}$, the loop was opened. This also

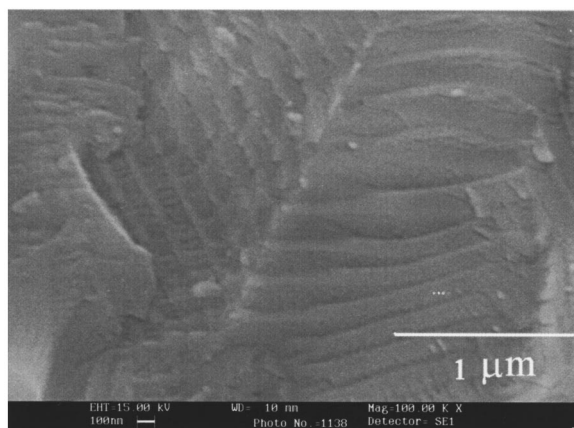


FIG. 4. SEM micrograph of a ceramic fiber cross section.

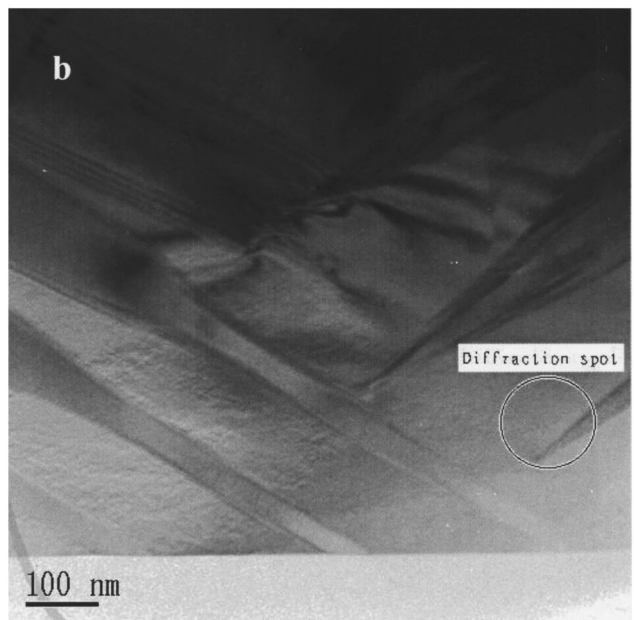
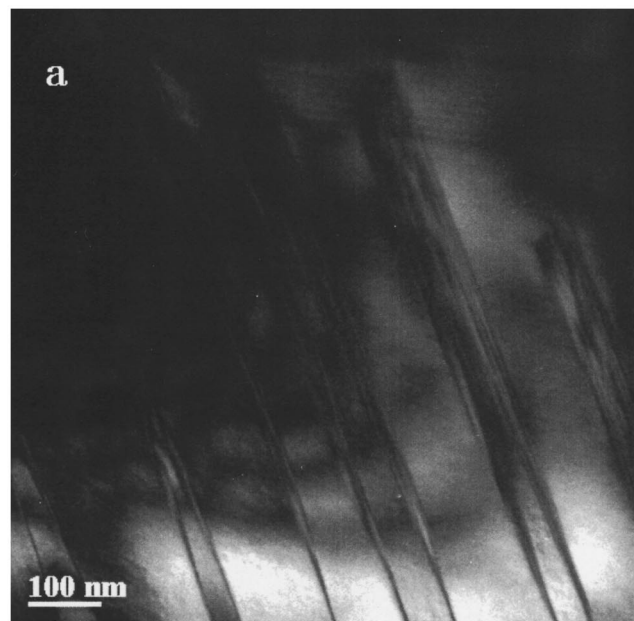


FIG. 5. TEM micrograph of a PSmT ceramic fiber.

can be explained from the cramping effect of the layer structure 90° domains. Figure 9 shows the hysteresis loop of 1-3 composites under alternating current of different frequency at room temperature. The loops become narrower as the frequency increases. These samples can withstand an electric field of up to $15\ \text{kV/mm}$. This electric field is much higher than what a normal ceramic could withstand.

The PSmT fiber/epoxy 1-3 composite disks were poled under an electric field of $4.5\ \text{kV/mm}$ at 115°C for 15 min before they were cooled to room temperature with the field kept on. Then they were wrapped in aluminum foil and aged for two days. The piezoelectric constant d_{33} was measured by a d_{33} meter. According to the IEEE Standard on piezoelectricity, ANSI/IEEE Std 176-1987,⁷ the electromechanical coefficient k_t and dielectric permittivity ϵ of the composites

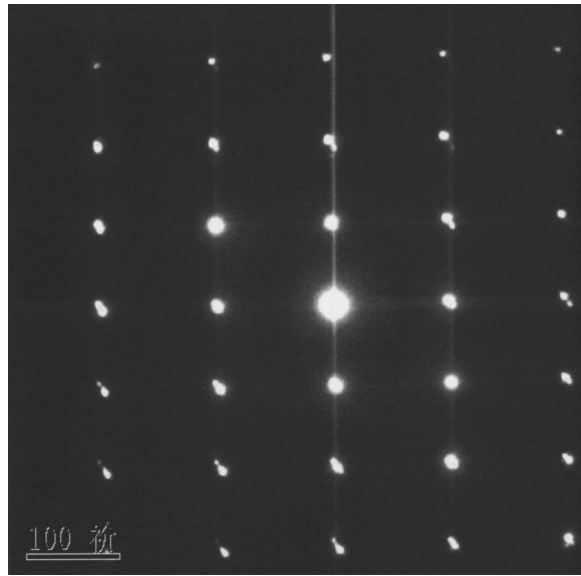


FIG. 6. Electron diffraction patterns of a PSmT ceramic fiber.

were measured by an impedance analyzer model HP4294A at room temperature. The d_{33} , k_t , and ϵ for the PSmT fiber/epoxy 1-3 composites with 0.68 volume fraction of PSmT fibers were 48 pC/N, 0.51, and 118, respectively.

In ceramics, the grains are randomly oriented. Spontaneous polarizations of the domains are also oriented along different directions. In the poling process, spontaneous polarization of the domains will be switched under the high electric field. PSmT ceramic has a tetragonal crystal structure. The structure may be regarded as consisting of TiO_6 octahedra surrounded by Pb^{2+} (or Sm^{3+}) cations.⁸ Considering the lattice site of the ions, dipole direction of the domains normally can be switched by 180° or 90° . According to the x-ray diffraction patterns of the ceramic fiber, the calculated parameters of the PSmT crystal cell were $a = 3.899 \text{ \AA}$, $c = 4.054 \text{ \AA}$. When the polarization of the domain switches by 180° , the shape (a and c axes) of the unit cell will only change slightly. If the polarization of the domain switches by 90° , the original a axis of unit cell will

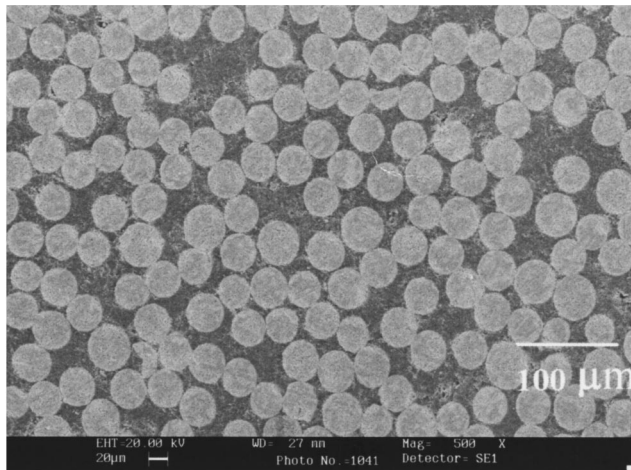


FIG. 7. SEM micrograph of a PSmT ceramic fiber/epoxy 1,3 composite.

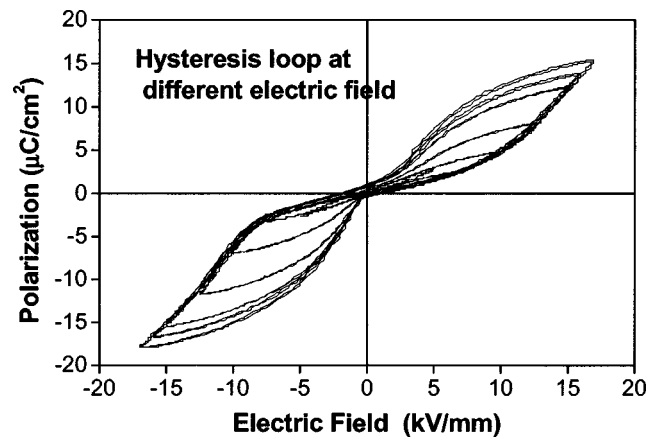


FIG. 8. Hysteresis loop of a PSmT ceramic fiber/epoxy 1,3 composite, measured under 5 Hz alternating electric field.

change into the c axis. The size and shape of the cell will also change. The shape of the relative domain will change too. But the clamping effect of the layer structure 90° domains makes it difficult to change the shape of the domains. So PSmT ceramic has a high coercive electric field.

Compared with pure PT, manganese ions have a similar radius as Ti^{4+} and substitute Ti^{4+} ions at the B site. The radius of Sm^{3+} ions is much larger than Ti^{4+} , but smaller than Pb^{2+} . Samarium ions in PSmT take the place of some lead ions at the A site. According to the electric balance in crystal structure, every two Sm^{3+} ions will substitute three Pb^{2+} ions. Some A site vacancies were formed. Due to the smaller radius of the Sm^{3+} and the A site vacancies in the crystal structure, the parameters of PSmT unit cell changed from $a = 3.894 \text{ \AA}$ and $c = 4.140 \text{ \AA}$ (of pure PT) to $a = 3.899 \text{ \AA}$ and $c = 4.054 \text{ \AA}$. The c/a ratio changed to 1.04. On the other hand, some A site vacancies broke the balance of the electric field of cations. So, domain switching in PSmT is a little easier than that in pure PT.

Compared with PZT ceramics, PSmT ceramic has a lower relative permittivity. According to the polarization mechanism, dielectric properties of the ionic crystal under low electric field are usually regarded as ionic displacement and electron displacement. In doped PT and PZT systems,

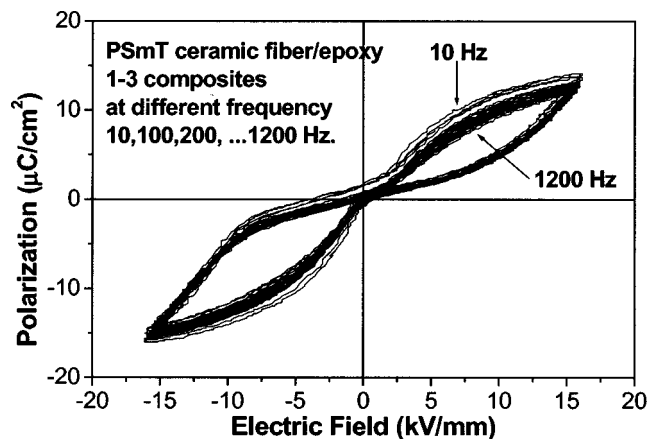


FIG. 9. Hysteresis loop of a PSmT ceramic fiber/epoxy 1,3 composite, measured at different frequency.

the radius of the lead and oxygen ions was large. So the electronic cloud distortion of these ions was larger than that of the other ions. Ti^{4+} and Zr^{4+} ions having a small size and more electric charge are placed in the center of the octahedron. Ionic displacement in polarization mainly results from these ions. Comparing the composition and the crystalline structure of doped PT with PZT, the main reason for their different relative permittivity may be on the difference in the crystalline structure. Doped PT has a tetragonal structure. The c/a ratio is in the region of 1.04–1.06. Doped PZT has a rhombohedron or tetragonal structure, depending on the Zr/Ti ratio. The c/a ratio is only 1.00–1.02.⁹ Ionic displacement under low electric field is related to their occupied space. Under the same electric field, the larger the space is, the more their displacement will be. In the tetragonal structure of doped PT ceramic, there is a small spacing along the a axis, so the displacement in this direction should be small. The c axis of the doped PT is longer than the a axis; but spontaneous polarization made the Ti^{4+} ions deviate to one side of the octahedron. The extent of further displacement under a low electric field is small. In PZT ceramic with a pseudocubic or rhombohedral structure, a and c values are almost the same. There is a large freedom for Ti^{4+} (or Zr^{4+}) displacement in three dimension. So doped PT ceramics have a lower relative permittivity than that of PZT. Furthermore, the same reason can explain that PZT ceramics with a composition near the morphotropic phase boundary have a larger relative permittivity.

IV. CONCLUSION

PSmT ceramic fibers were prepared by the sol-gel method. These fibers can withstand higher electric field.

Layer structure 90° domains were found in the ceramic fibers by SEM and TEM. The hysteresis loop of PSmT ceramic fiber/epoxy 1-3 composites was measured under a higher field at room temperature. It was found that these samples could withstand an electric field up to 15 kV/mm. The piezoelectric properties of the composite were also measured. For the PSmT fiber/epoxy 1-3 composites with 0.68 volume fraction of fibers, the piezoelectric constant d_{33} , electromechanical coefficient k_t , and relative dielectric permittivity ϵ were 0.51, 48 pC/N, and 118, respectively.

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