Enhancement of nonvolatile polarization and pyroelectric sensitivity in lithium tantalate (LT)/poly(vinylidene fluoride) (PVDF) nanocomposite

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Abstract

We report the ferroelectric and pyroelectric properties of the composite films of lithium tantalate (LT) nanoparticle in poly(vinylidene fluoride) PVDF matrix at different volume fractions of LT ($f_{LT} = 0.047, 0.09$ and $0.17$). For an applied electric field of $150 \text{ kV cm}^{-1}$ the nonvolatile polarization of the composite was observed to increase from $0.014 \text{ } \mu\text{C m}^{-2}$ at $f_{LT} = 0$ to $2.06 \text{ } \mu\text{C m}^{-2}$ at $f_{LT} = 0.17$. For $f_{LT} = 0.17$, the composite films exhibit a saturated ferroelectric hysteresis loop with a remanent polarization ($P_r = 4.13 \text{ } \mu\text{C cm}^{-2}$). Compared with pure poled PVDF the composite films also showed a factor of about five enhancement in the pyroelectric coefficient at $f_{LT} = 0.17$. When used in energy detection mode the pyroelectric voltage sensitivity of the composite films was found to increase from $3.93$ to $18.5 \text{ V J}^{-1}$ with an increase in $f_{LT}$ from $0.0$ to $0.17$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Single crystal, ceramic and polymeric pyroelectric materials (such as TGS, LiTaO$_3$, lead zirconate titanate (PZT) and poly(vinylidene fluoride) PVDF) are extensively used as thermal infrared detectors because these materials offer the advantages of good sensitivity, room temperature operation and low cost [1]. More recently there has been considerable interest in the use of ferroelectric ceramic/polymer composites for piezoelectric and pyroelectric sensor applications as the composites can combine the mechanical compliance and flexibility of polymers with the high piezoelectric and pyroelectric properties of ceramics [2]. However, since the permittivity of ceramic is much greater than that of the polymer matrix, the local electric field on ceramic materials is very small and therefore ensuring an efficient polarization of dipoles in the ceramic/polymer composites is often a challenge [3, 4]. Poling for a long period of time (1 h or longer) at elevated temperatures and with the use of a high dc field (1 MV cm$^{-1}$) is usually used to align the ceramic phase [2]. Dielectric breakdown of the sample is often the problem in such situations. The corona discharge technique and stepwise poling procedure have also been used to improve the poling behaviours of ceramic particles. Sakamoto et al showed that by the addition of 1 vol% of graphite in lead zirconate titanate (PZT)/polyurethane (PU) composite the poling process becomes more effective and leads to an increase in the pyroelectric coefficient [3] because the carbon particles create a continuous electric flux path between PZT grains.

Several theoretical models have been developed to understand the influence of the electrical conductivity and poling time on the pyroelectric properties of composites. These show the important role of interfacial charge in the poling process [5–7]. It has been established that if the poling time is longer than the relaxation time of interfacial charge, the ceramic phase can be fully polarized even though the local...
field on ceramic particle is very small [7]. The result of the studies carried out by Zhang et al shows the need to control both the electrical conductivity and the dielectric constants of the constituents of the composite. While for the lower conductivity range an increase in conductivity of the matrix phase can lead to significant enhancement in the pyroelectric coefficient [8], beyond a certain value the increase in leakage current and the resulting dielectric loss becomes detrimental to the poling process. The dielectric constant of the matrix or constituent places a limit on the applications ferroelectric composites for device point of view.

A major drawback with the use of PVDF as sensor material is the requirement of a high poling field. We have therefore investigated the PVDF and lithium tantalate (LT) composites for their ferroelectric, pyroelectric and dielectric properties. The choice of LT was dictated by the fact that while compared with PVDF it has a much lower poling field requirement and a larger pyroelectric coefficient, its dielectric constant is comparable to PVDF. Our studies show that LT/PVDF nanocomposite can prove to be a better alternative to both single crystal LiTaO3 and pure PVDF for pyroelectric sensor applications.

2. Experiment

Nanoparticles of LT were prepared by the sol–gel process through the alkoxide route. Spherical and nonaggregated nanoparticles (20–40 nm) of LT were obtained by adding oleic acid (capping ligand) [9] to the sol of LT. These nanoparticles were dispersed in a PVDF solution that was prepared using dimethyl sulphoxide (DMSO) solvent at 90 °C. The LT/PVDF composite films were cast on glass at the same temperature. Free standing films of thickness 30 µm were obtained and annealed at 90 °C for 5 h. In order to study the change in ferroelectric polarization behaviour with the volume fraction of the filler LT/PVDF composite films with different volume fractions of LT were prepared. The phases of composite, the microstructure and the electric properties were studied using x-ray diffraction, scanning electron microscopy (SEM), atomic force microscopy (AFM) and an HP 4194A impedance analyzer [10].

The ferroelectric hysteresis properties were studied using a ferroelectric loop tracer (RT6000 of Radiant Technologies) at 1 Hz. Pulsed polarization positive up-negative down (PUND) measurements were used to extract the real switch polarization (ferroelectric polarization) of the LT/PVDF composites. In figure 1(a) we show the PUND waveform applied to the sample and the measured parameters. The PUND characterization measurement was made based on a series of five pulses. The initial pulse was used to preset the sample to the polarization state. No measurement was made as a result of this pulse. The second pulse switches the sign of the polarization and measures the amount of polarization switched. After the measurement, the sample was returned to zero volts and allowed to settle so that all volatile polarization switching dissipates. After this period, a second measurement was made at 0.0 V. The third pulse was a twin of the second, and the same measurements were made. In this case, the sample was not switched, so that the measured polarization will represent the volatile component (parasitic + leakage) of the sample. The fourth and fifth pulses mirror the second and third, switching the sample in the −1Vmax direction. Both the switching and the nonswitching measurements were made just as described for pulses two and three. The PUND measurement establishes eight parameters, commonly found in the ferroelectric literature. Polarization being measured with each pulse has been shown in figure 1(b). Here P∗ corresponds to total polarization (volatile and nonvolatile) and P∧ is the volatile component of polarization (parasitic effect + leakage effect). The difference dP = P∗ − P∧ = 2P provides the value of nonvolatile polarization arising due to ferroelectricity.

For the measurement of the pyroelectric coefficient the PVDF and LT/PVDF composite films were used for the fabrication of pyroelectric sensors which could be operated in total pulse energy measurement mode. When a pulse (~17 ns) from a Nd: YAG laser (that was used for the measurement of pyroelectric voltage sensitivities of the sensors) falls on the front gold electrode of the sensors, approximately 2% of the pulse was absorbed by the sensor due to gold coating. The rest of the energy gets reflected from the gold surface. The absorbed energy increases the temperature of the sensor, which in turn changes the polarization of the material. The current arising due to the change in polarization with respect to time flows in the circuit. The output voltages corresponding to different input energies of laser pulses were recorded. The pyroelectric voltage sensitivities and the pyroelectric coefficients of the composite films were calculated from the recorded voltages [11]. It is pertinent to note that the method used by us for the measurement of the pyroelectric coefficients of the films is expected to be more accurate than the determination of the pyroelectric coefficient by direct heating of the film because heating of PVDF may change the phases present in it.

3. Results and discussion

The presence of β-PVDF and LT nanoparticles in the composite films was confirmed by the x-ray diffraction patterns [10]. As the volume fraction of LT nanoparticles increases in the LT/PVDF composite films the network of nanoparticles increases along all directions. The dielectric constants of the composite films at 1 kHz were measured to be 20.26, 24, 28.8 and 48 for фLT = 0.00, 0.047, 0.09 and 0.17, respectively [10].

In figure 2, we show the P–E hysteresis loop of pure and composite PVDF films. At an applied electric field of 400 kV cm−1 at 1 Hz the polarization was 0.17 μC cm−2 for pure PVDF (figure 2(a)) and for composites it increased to 0.23 μC cm−2 for фLT = 0.047 (figure 2(b)) and to 1.04 μC cm−2 for фLT = 0.09 (figure 2(c)). From the hysteresis loop (figure 2(c)) it can also be seen that in the low frequency range the dielectric loss increases as the volume fraction of LT increases. PUND measurements were therefore carried out to get a proper estimate of nonvolatile polarization of composite thin films (discussed in the next section). For фLT = 0.17, a sharp increase in polarization was observed (figure 2(d)). At an applied field of 170 kV cm−1,
while the polarization of pure PVDF is almost negligible (0.05 μC cm$^{-2}$), for films with $f_{LT} = 0.17$ its value is 2.6 μC cm$^{-2}$. It is pertinent to note that to achieve polarization of 2.6 μC cm$^{-2}$ in pure PVDF, one would have to apply more than 1000 kV cm$^{-1}$ [12].

In figure 3 we show the results of (PUND) measurement on pure and composite PVDF films. One can see from figure 3(a) that for pure PVDF the nonvolatile polarization ($dP = P^* - P^\wedge = 2P_r$) starts to increase beyond 100 kV cm$^{-1}$ and reaches 0.25 μC cm$^{-2}$ at 400 kV cm$^{-1}$, which is less than the 2$P_r$ value (0.34 μC cm$^{-2}$ at 400 kV cm$^{-1}$) observed in hysteresis analysis. This shows that for pure PVDF the nonvolatile polarization ($P_r$) is 0.125 μC cm$^{-2}$ at an applied field of 400 kV cm$^{-1}$.

For the composite film with $f_{LT}$ of 0.047, the nonvolatile polarization starts to increase beyond 100 kV cm$^{-1}$ (figure 3(b)) and becomes 0.43 μC cm$^{-2}$ at 400 kV cm$^{-1}$, which is nearly equal to the 2$P_r$ value measured by hysteresis (0.46 μC cm$^{-2}$ at 400 kV cm$^{-1}$). For $f_{LT} = 0.09$, the nonvolatile polarization ‘$dP$’ is 2.05 μC cm$^{-2}$ at 400 kV cm$^{-1}$ (figure 3(c)), which is consistent with the 2$P_r$ values obtained from hysteresis (i.e. 2.08 μC cm$^{-2}$ at 400 kV cm$^{-1}$ for $f_{LT} = 0.09$). Similarly for $f_{LT} = 0.17$, the nonvolatile polarization is 4.13 μC cm$^{-2}$ at 150 kV cm$^{-1}$ (figure 3(d)), which is less than the 2$P_r$ values obtained from hysteresis (4.4 μC cm$^{-2}$ at 150 kV cm$^{-1}$ for $f_{LT} = 0.17$). At 150 kV cm$^{-1}$ the polarization of pure PVDF is 0.0142 μC cm$^{-2}$ (figure 3(a)). From PUND measurement it is clear that the intrinsic polarization is due to ferroelectricity and not due to leakage. PUND measurements also show that the ferroelectric polarization increases significantly from 0.0142 μC cm$^{-2}$ for pure PVDF to 2.06 μC cm$^{-2}$ for the LT/PVDF ($f_{LT} = 0.17$) composite at an applied field of 150 kV cm$^{-1}$.

The maximum coercive field for single crystal LT is 200 kV cm$^{-1}$ [13]. When the volume fraction of LT increases

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**Figure 1.** (a) Standard PUND test wave form and controlling parameters. (b) Polarization being measured with each pulse.
Figure 2. $P-E$ hysteresis loop of (a) pure PVDF and of LT/PVDF composites for $f_{LT} = (b) 0.047$ (c) 0.09 and (d) 0.17.

In order to verify the pyroelectric properties of the LT/PVDF composite films, pyroelectric sensors were fabricated from these films. By operating these in laser energy meter mode, pyroelectric voltages generated at constant energy of laser pulse were recorded from these films. For energy meter application, the pulse width of laser ($w$) should be very much less than the thermal time constant [16]. This requires that the thickness of the sensor be much greater than the diffusion depth so that during the radiation pulse little heat will flow out of the rear surface of the ferroelectric. In this condition the output voltage of the sensor can be expressed as

$$V_0(t) = \left(\frac{Ap}{C'cd}\right) \left(\frac{1}{C}\right) e^{-t/\tau_e} \left(A \int_0^w F(t) \, dt\right),$$

where $\tau_e = RC$, the electrical time constant of the circuit and $w$ is the pulse width of the source. $F(t)$ is the space-averaged energy flux per unit area absorbed by the detector, $p$ is the pyroelectric coefficient of the material, $A$ is the active area of the sensor, $c$ is the volume specific heat of the material and $d$ is the thickness of the sensor material.

If the electrical time constant is long compared with the duration of the incident signal, and $\tau_e \gg w$ then equation (1) simplifies to

$$V_0(t) = \left(\frac{Ap}{C'cd}\right) \left(\frac{1}{C}\right) e^{-t/\tau_e} E.$$  

In PVDF, the application of a high field is difficult due to an increase in the leakage current which arises due to the increase in the network of nanoparticles. At high field (greater than 4000 kV cm$^{-1}$) the PVDF may show high polarization but direct poling of thin PVDF film is always prone to damage of the thin film. The addition of LT nanoparticles (volume fraction 0.17) leads to a reduction in the poling field and a large nonvolatile polarization ($2.06 \mu C \cdot cm^{-2}$) that is comparable to saturation polarization of triglycine sulphate ($2.8 \mu C \cdot cm^{-2}$) at room temperature [14]. However, the polarization observed in the composite with $f_{LT} = 0.17$ at 150 kV cm$^{-1}$ is small compared with remanent polarization ($7 \mu C \cdot cm^{-2}$) of the pure PVDF thin film at the maximum applicable field (4000 kV cm$^{-1}$) [15].
If input energy of the pulse falls on the coating material (coated on pyroelectric material), then equation (3) can be written as

\[ V_0(t) = \left( \frac{p}{c'd} \right) \left( \frac{1}{C} \right) \text{e}^{-t/\tau} \eta E, \]  

\[ V_0(t) = \left( \frac{p}{c'\varepsilon_A} \right) \left( \frac{1}{\varepsilon_0\varepsilon_r} \right) \text{e}^{-t/\tau} \eta E, \]  

\[ V_0(t = 0) = \left( \frac{p}{c'\varepsilon_A} \right) \left( \frac{1}{\varepsilon_0\varepsilon_r} \right) \eta E, \]

where \( C = C_s \) capacitance of the sensor material, \( \varepsilon_r \) is the dielectric constant of the material and \( \varepsilon_0 \) is the permittivity of free space.

In figure 4(a) we show the output signal generated from pure and composite PVDF films when Nd:YAG laser pulse (17 ns, 2.6 mJ) falls on these sensors. The magnitude of the generated output voltage from 11.31 to 49 mV as \( f_{LT} \) increases from 0 to 0.17. The pyroelectric voltage sensitivity of the PVDF composite films can be seen to increase from 3.9 to 18.5 V J\(^{-1}\) as the volume fraction of LT increases from 0.0 to 0.17. The pyroelectric coefficients of the PVDF and LT/PVDF composites were calculated using equation (6). The values of the pyroelectric coefficient were found to be 0.128 \( \times \) 10\(^{-8}\) C cm\(^{-2}\) K\(^{-1}\) and 1.47 \( \times \) 10\(^{-8}\) C cm\(^{-2}\) K\(^{-1}\), respectively, for \( f_{LT} 0.0 \) and 0.17. The reported pyroelectric coefficient of pure PVDF film is (0.27–0.439) \( \times \) 10\(^{-8}\) C cm\(^{-2}\) K\(^{-1}\) [17, 18].

Why is ferroelectric polarization of the LT/PVDF composite film larger than that for pure PVDF? Ferroelectric nanoparticles smaller than the ferroelectric domain have a single domain structure [19, 20]. The characteristic ferroelectric to paraelectric transition temperature (Curie temperature) decreases as the particle size of the ferroelectric material decreases. In the case of nanoparticles, there is no long range ferroelectric order. The energy barrier separating alternative polarization states of the nanoparticle decreases as the size decreases. The size effect is more prominent when the size of the nanoparticle is below 10 nm. The LT nanoparticles of size 20–40 nm (which have been used to make composite films) are ferroelectric and the Curie temperature of these particles is \(~492\) °C [9]. For volume fraction of LT 0.047 in PVDF matrix, the distribution of nano-agglomeration is random, resulting in a random distribution of polarization directions and the effective applied field on the nanoparticles is very less due to the screen effect of polymer. Therefore, there is only a small increase in the nonvolatile polarization. As the volume fraction of LT increases in the PVDF matrix the cooperative interaction between nanoparticles increases and the screening effect on the nanoparticle is less when the volume fraction of LT is more in composite films. This in turn increases the effective applied field on nanoparticles.

The maximum coercive field of LT is 200 kV cm\(^{-1}\) regardless of the stoichiometry of LT. The spontaneous polarization of LT is 60 µC cm\(^{-2}\) at an applied field of 200 kV cm\(^{-1}\). But a high field (1200 kV cm\(^{-1}\)) is required to pole the PVDF film. Therefore, in comparison with PVDF crystalline regions, at a small applied field, the LT nanoparticles in composite films get easily poled. Thus as the LT volume fraction increases more nanoparticles get poled and the nonvolatile polarization increases. This would explain the observed large increase in ferroelectric polarization (from 0.014 µC cm\(^{-2}\) for pure PVDF to 2.06 µC cm\(^{-2}\) for LT/PVDF (\( f_{LT} = 0.17 \)) at an applied field of 150 kV cm\(^{-1}\).

4. Conclusion

The ferroelectric polarization and the pyroelectric coefficient of LT/PVDF nanocomposite films increase with increase in the volume fraction of LT in LT/PVDF. The LT/PVDF composite film can be poled by applying a low field. In view of the fact that the growth of LT single crystal is very difficult and large fields are required to pole PVDF, the LT/PVDF composites due to the lowered poling field and higher polarization as compared with PVDF appreciably should prove an attractive material for pyroelectric sensor application.

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