PVDF-PZT-5H Composites Prepared by Hot Press and Tape Casting Techniques

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ABSTRACT: Piezoelectric polymer–ceramic composites are promising materials for transducer applications, and they are widely used in underwater hydrophones, biomedical imaging with ultrasound, and nondestructive testing applications. The critical factor in the 0–3 composite is to ensure homogeneous distribution of the filler in the matrix. To ensure this objective, PVDF-PZT composite was prepared by two different routes: hot press and tape casting techniques. Loss on ignition and scanning electron microscopy studies were conducted to find out the uniformity of the composites prepared. It is found that hot press technique gives better uniformity compared to tape casting technique. PZT concentration was varied from 20 to 60 vol %. Physical and dielectric properties were studied. FT-IR, DSC, and XRD characterization studies of PVDF were also recorded. Density of the composites was 2.74 to 5.13 g/cm^3 as PZT concentration increased from 20 to 60 volume fractions. The dielectric constant of composites at 1 MHz varied from 16.74 to 98.48 as PZT concentration increased from 20 to 60 volume fractions. Hot press technique that combines solution and melt processing was found to be the better method for the preparation of 0–3 composites. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 146–151, 2007

Key words: composites; dielectric properties; density; electron microscopy; fillers

INTRODUCTION

Piezoceramics with high pyro and piezoelectric constant are widely used in transducer and many other applications. Piezoelectric polymers are used in applications where acoustic impedance matching to that of water or living tissue is required. The important factor for these applications is figure of merit ($d_h g_h$). Piezoceramics are fragile, inflexible, and hence the processability is difficult, while piezopolymer have low piezoelectric coefficients. Polymer–ceramic composites combine superior properties of both polymer and ceramic phases, which offers many advantages over those of the constituent materials. Many types of transducers of piezoceramic–polymer composites have been widely used in several applications, such as hydrophones and biomedical transducers.[1–7] These diphasic composites have better mechanical shock resistance, better compliance, etc. The figure of merit of composites is far superior compared to the constituents. Most widely studied composites are that consists of PVDF or its copolymers and PZT powder.[8–13] A steady rise is reported in the demand for the polymer–ceramic piezocomposites.[14]

The 0–3 connectivity composite in which ceramic fillers are uniformly distributed in the polymer matrix is the simplest form of the composite. The major advantage of these composites is their ease of fabrication into variety of shapes; flexible thin film, extruded bars, fibers, and molded shapes. In 0–3 composites, the critical factor is to ensure homogeneous distribution of the filler in the matrix. Different preparative techniques such as melt processing to solution casting are used to fulfill this objective.[8–13]

In the present study, PVDF-PZT composites have been prepared by an unconventional route, which combines the solution and melt processing technique to ensure uniform distribution of filler. A comparative study of hot press and tape casting technique were done with respect to physical and dielectric characteristics of the composites with varying ceramic contents (20–60 vol %).

EXPERIMENTAL

Raw materials

PVDF of number-average molecular weight 71,000 supplied by Sigma Aldrich, USA, PZT-5H powder supplied by Sparkler ceramics, India, and dimethyl formamide (DMF) supplied by Merck, India, were used in this study.

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Preparation of PVDF-PZT composites

Hot press technique

Hot press method combines solution and melt processing techniques. PVDF was dissolved in DMF and the solution is concentrated to get an optimum viscosity for the loading of ceramic powder. PZT powder was added and stirred well to get a uniform distribution of the filler. The prepared slurry of PVDF-PZT-5H was then coagulated by the addition of nonsolvent and dried. The composite discs were made by thermolamination of the coagulated mass under optimized conditions of temperature and pressure. The volume percentage of PZT powder was varied from 20 to 60%.

Tape casting technique

PVDF-PZT solution was prepared as described in hot press technique. A well-dispersed and concentrated solution is degassed and spread on a flat moving carrier surface using double doctor blade process. A thin sheet of high uniformity is formed, and the solvent is evaporated leaving the dried tape with sufficient strength and flexibility. These tapes are cut into proper shape (thin circular sheets), stacked, and laminated similar to hot press technique.

Characterizations

Uniformity of the filler material was measured by taking pieces from different parts of the laminated composite and ignited at 600°C for 1 h and measuring loss on ignition. From this, volume fraction of PZT at various places of the laminate was calculated. The uniformity was further confirmed using scanning electron microscopy (SEM, Philips XL-30).

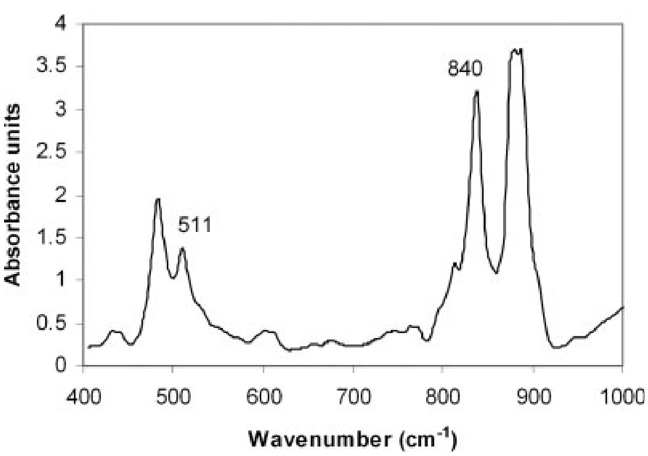

Figure 1 FT-IR of casted PVDF film.

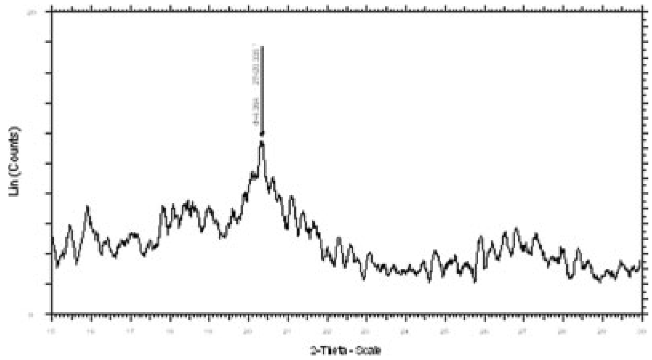

Figure 2 XRD pattern of PVDF film.

The virgin PVDF was characterized using FT-IR (Tensor 27, Brucker), XRD (AXS, Brucker), and DSC (Q_{100}TA Instruments).

The sample was coated with air-drying silver paste for dielectric measurements. The dielectric properties were measured using Impedance analyzer (HP 4192A) in the range of 100 Hz to 10 MHz. The a.c. conductivity (σ_{ac}) was calculated using the relation,

$$\sigma_{ac} = \varepsilon_0 \omega \varepsilon' \tan\delta \quad (1)$$

where "ε_0" is the permittivity of the free space (8.85 $\times 10^{-12}$ Fm^{-1}), "ε'" is the dielectric constant of the composite, tan δ is the dissipation factor, and "ω" the angular frequency, which is equal to $2\pi f$ where "f" is the frequency in hertz.

RESULTS AND DISCUSSION

Characterization of PVDF with 0% filler

Figure 1 shows the FTIR of PVDF sample. The absorptions at 840 and 511 cm^{-1} are the characteristic absorption peaks of β -PVDF.[8–9] The characteristic peak of α-PVDF (766, 795, 856, and 976 cm^{-1}) and γ-phase (778, 812, and 834 cm^{-1}) are absent.[8] This shows that PVDF formed is predominantly β-phase. The XRD pattern of the PVDF sample (Fig. 2) shows the major peak at 20.3, which is the prominent peak of β-PVDF.[9]

From the DSC analysis (Fig. 3) it is found that the melting point of the PVDF film casted from DMF solvent was 172.19°C. No other transition peak was shown in the region of the measurements.

Physical properties of PVDF-PZT-5H composite

Loss on ignition

To understand the uniformity of filler distribution for the composites obtained, loss on ignition at different areas of the composites were measured, and the values are given in Table I. It is found that the

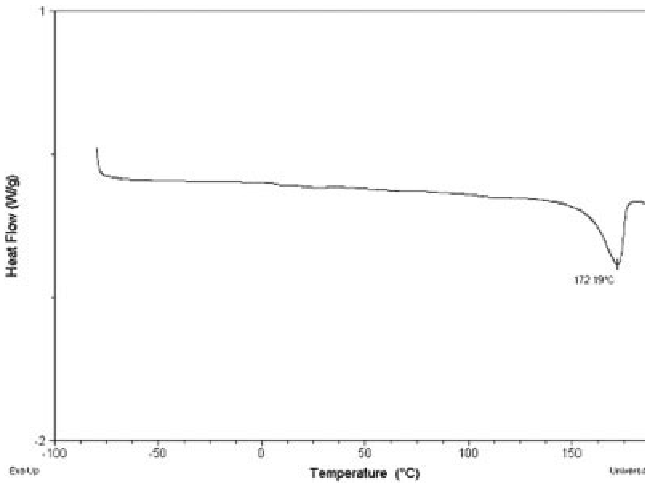

Figure 3 DSC of casted PVDF film.

PZT powder is almost uniformly distributed in the PVDF matrix for the composites prepared by hot process technique. This is further confirmed by SEM studies. The SEM photograph of PVDF-PZT at 20, 40, and 50 vol % are given in Figure 4(a–c), respectively. As the volume fraction of PZT content increases, uniformity is slightly reduced. This is because the chances of settling of PZT powder at higher volume fraction are more. In the case of tape casting technique, the filler concentration is uniform at lower PZT volume fractions. But at higher volume fractions the settling of PZT powder is high in the tape casting technique, since during solvent evaporation time itself the PZT powder will start settling. The rate of settling can be reduced by using proper dispersing agents.

Density measurements

Density of the composites with varying volume percentage of PZT is given in Table II. Theoretical values of density of the composite were calculated using the eq. (2).

$$\rho = V_f \rho_f + (1 - V_f)\rho_m \quad (2)$$

where "ρ"is the density of the composites, "V_f" is the volume fraction of filler (ceramic), and "ρ_f" is density of filler, and "ρ_m" is the density of matrix (PVDF). Density of PZT is taken as 7.5 and density of PVDF as 1.7 g/cm^3 in the calculation.

It is found that the density increases with filler concentration, and it is slightly lower than theoretical density. Theoretical values were calculated with the assumption that there are no voids or defects in the composites. However, during the preparation, minor voids or defects will be formed which results in lower density. Compared to tape casting technique, nonsolvent method gives excellent dispersion of ceramic particles in the polymer matrix. As a result, porosity will be less in nonsolvent hot pressed samples and gives comparatively denser composite than tape casting route. At low concentration of PZT, density of the composites prepared through hot press and tape techniques shows close values, while at higher volume fraction, composites prepared by tape casting routes have lower density. In the tape casting process, at high filler loadings (>30 vol %), it is difficult to ensure uniform filler distribution: the ceramic particles may form aggregates and may tend to settle. This will cause some porosity in the samples, reducing density. A similar behavior was noticed in solvent casting of PVDF/PZT composites.[11] While hot press technique gives excellent dispersion even at high filler loadings, it produces dense composites with less porosity as evidenced from SEM images.

Dielectric measurements

The dielectric constant (ε') obtained for PVDF and PZT-5H at 1 MHz is 10.4 and 1590, respectively. The

TABLE I
Loss on Ignition at Various Places of the PVDF-PZ-5H Composites

PZT : PVDF (vol %)		Hot press			Tape casting		
		Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
20 : 80	PZT	19.97	19.95	20.36	20.26	22.65	21.75
	PVDF	80.02	80.04	79.63	79.73	77.34	78.35
30 : 70	P Z T	30.45	30.27	30.26	31.80	31.52	29.11
	PVDF	69.50	69.73	69.74	68.19	68.47	70.88
40 : 60	P Z T	41.30	41.30	41.80	41.80	42.24	43.39
	PVDF	58.70	58.70	58.10	58.19	57.75	56.60
50 : 50	P Z T	47.80	48.10	47.30	57.80	56.60	59.77
	PVDF	52.20	51.90	52.70	42.56	43.39	40.22
60 : 40	P Z T	62.03	62.28	64.52	60.85	60.05	62.20
	PVDF	37.96	37.71	35.47	39.14	39.44	37.79

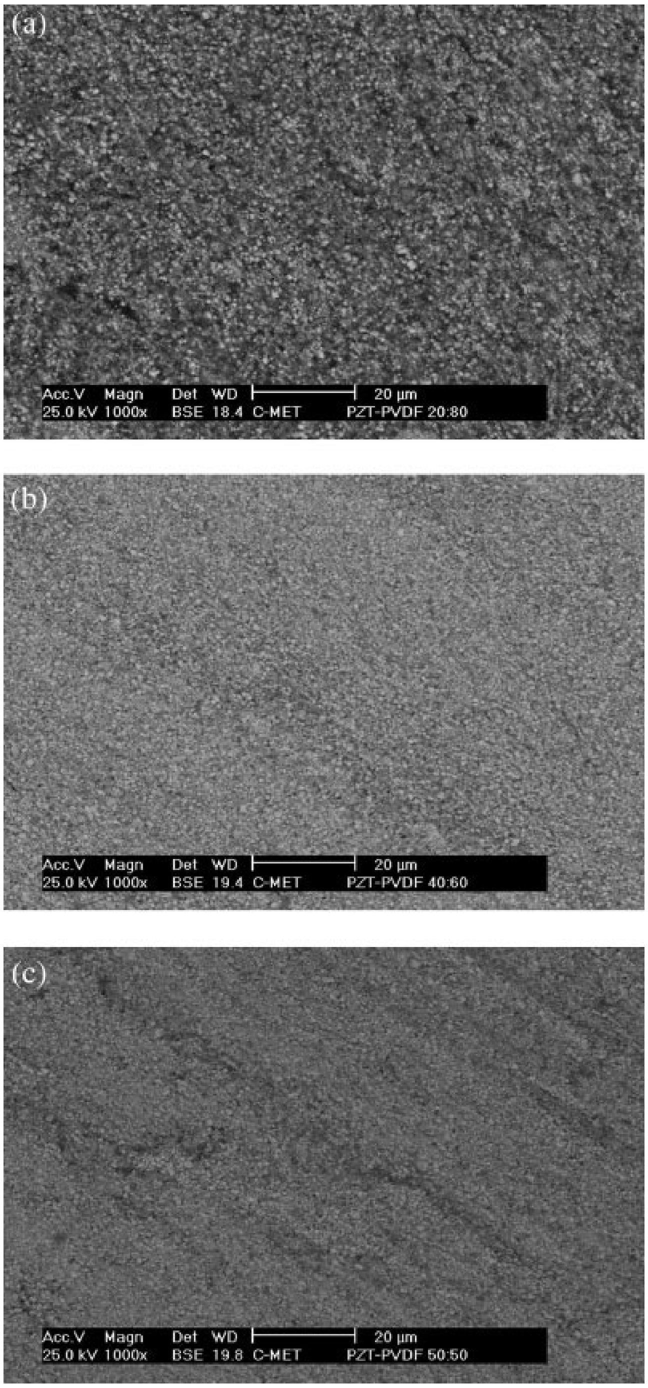

Figure 4 (a) SEM image of the composite with 20 vol % of PZT. (b) SEM image of the composite with 40 vol % of PZT. (c) SEM image of the composite with 50 vol % of PZT.

dielectric constant at 1 MHz of the composites prepared through hot press and tape casting is given in the Table III. The composites prepared through hot press technique have higher dielectric constant especially when PZT-5H concentration increased. At high volume fraction of PZT, the internal field generated by PZT favors orientation of PVDF dipoles and increases the ε′ value in both cases. The density of

TABLE II
Density of the PVDF-PZT-5H Composites

Volume percentage of PZT	Density		
	Theoretical	Hot press technique	Tape casting technique
20	2.96	2.74	2.74
30	3.65	3.41	3.51
40	4.21	3.99	4.13
50	4.85	4.50	4.43
60	5.47	5.13	4.59

TABLE III
Dielectric Constant of Composites at 1 MHz Frequency

Volume percentage of PZT	Dielectric constant at 1 MHz	
	Hot press technique	Tape casting technique
20	16.74	18.22
30	26.30	21.51
40	41.85	32.01
50	49.27	42.73
60	98.48	57.82

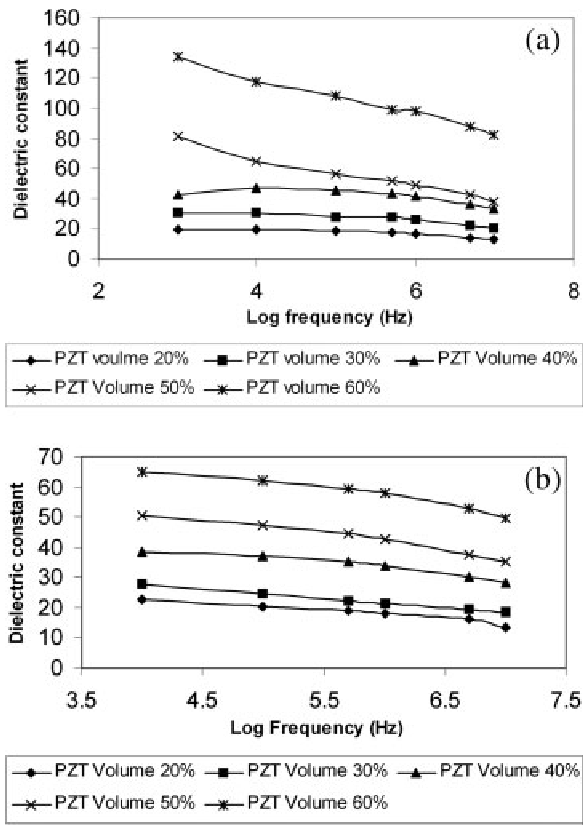

Figure 5 (a) Variation of dielectric constant with frequency for the composites prepared by hot press technique. (b) Variation of dielectric constant with frequency for the composites prepared by tape casting technique.

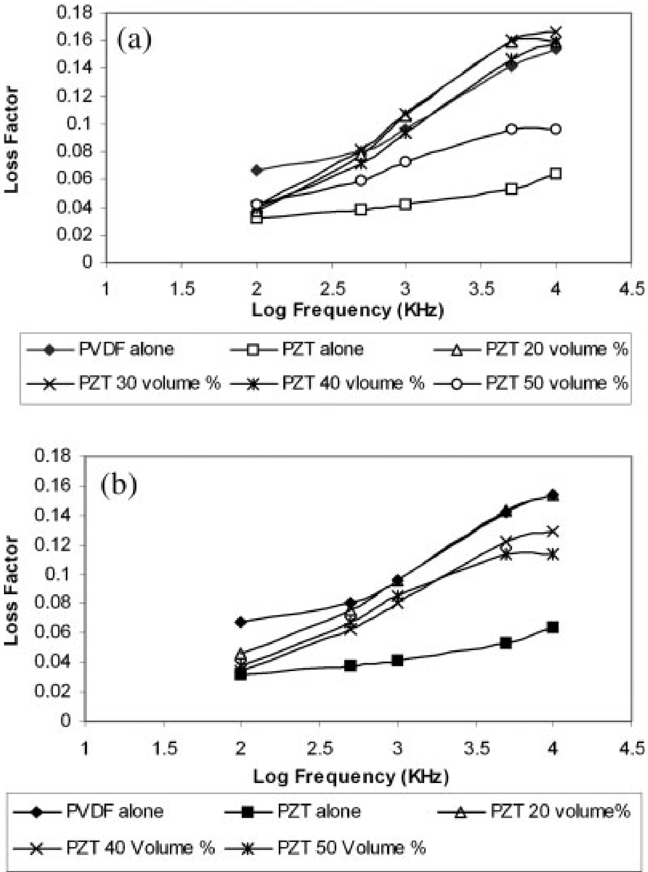

Figure 6 (a) Variation of dielectric loss with frequency for the composites prepared by hot press technique. (b) Variation of dielectric loss with frequency for the composites prepared by tape casting technique.

the composites affects the dielectric properties. As explained earlier, hot press technique gives denser composites compared to the tape casting process. This leads to better dielectric constant. For composites prepared by the tape casting method, porosity of the samples reduces the dielectric constant particularly at higher filler concentrations.[11] Porosity in samples hinders the orientation of dipoles, which ultimately reduces the dielectric constant.

The variation of dielectric constant with frequency for the composites prepared through hot press and tape casting techniques are shown in Figure 5(a,b), respectively. With increase in PZT content the dielectric constant of the composite increases at all frequencies. Maximum dielectric constant obtained at 1 MHz was 98.5 for 60 vol % of PZT. It is found that dielectric constant decreases as frequency increases especially at higher filler loading. But at high frequency region, a small decrease in the ε' value has been observed in all cases.

The frequency dependence of the dielectric loss is significant. The dielectric loss of the composites prepared through hot press and tape casting technique at various frequencies are given in the Figure 6(a,b), respectively. It is found that the minimum dielectric loss is observed for PZT disc at all frequencies and the maximum loss for PVDF samples. In the case of composites, the loss factor is found to be decreased with increase in PZT volume fraction. The loss factor is increased with frequencies in all the systems. Studies by Dias et al. reveals that dielectric relaxations in polymer–ceramic composites reflect those of the constituent materials.[6] In the case of PVDF-PZT-5H composite, the increase in loss factor mainly observed at higher frequency range is attributed to the losses caused by the movement of domain walls in the ceramic materials and also to the orientation of the dipole moments in PVDF.[8] The dielectric loss of the PVDF-PZT-5H composites observed to be dominated by those of the polymer, whereas the ceramic phase has a significant contribution on the steady-state electrical conduction.[15]

The variation of a.c. conductivity with frequency in hot press samples was given in Figure 7(a). The a.c. conductivity (σ_{ac}) was calculated using eq. (1).

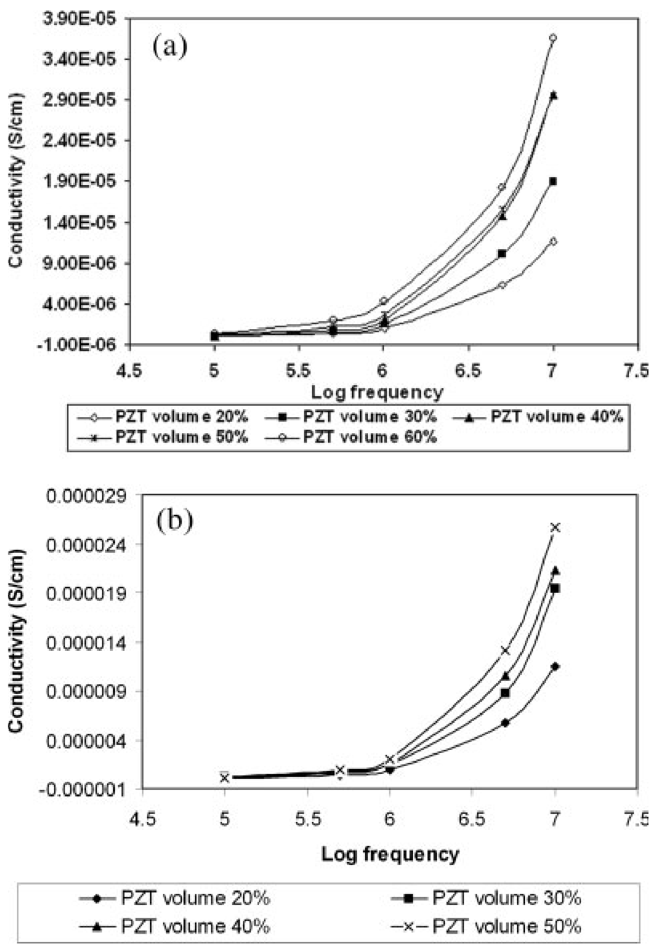

Figure 7 (a) Variation of a.c. conductivity with frequency for the composites prepared by hot press technique. (b) Variation of ac conductivity with frequency for the composites prepared by tape casting technique.

The conductivity is found to be increasing with increase in frequency and concentration of PZT, as a consequence of the decrease in relaxation time. Tape-casted composite also shows a similar trend [Fig. 7(b)].

CONCLUSIONS

PVDF matrix of the PVDF-PZT-5H composite is predominantly in the β-phase. Uniform distribution of filler in the matrix was obtained by using the hot press technique compared to tape casting technique. The dielectric constant of the composite increases with filler loading and dielectric loss is only marginally changed with filler concentration. The dielectric constant of the composites decreases as the frequency increases. The dielectric characteristic of the composites prepared through hot press technique shows better results compared to tape casting technique. The a.c. conductivity (σ_{ac}) is found to be increasing with increase in frequency and concentration of PZT.

References

1. Safari, A. J Phys III France 1994, 4, 1129.
2. David, M. M.; Stephen, W. S. IEEE Trans Ultra Ferro Freq Control 1999, 46, 961.
3. Nhuapeng, W.; Tunkasiri, T. J Am Ceram Soc 2002, 85, 700.
4. Schaeffer, R. P.; Janas, V. F.; Safari, A. IEEE Ferroelectrics 1996, 2, 557.
5. Tandon, R. P.; Singh, R.; Singh, V.; Swamiand, N. H.; Hans, V. K. J Mater Sci Lett 1992, 11, 883.
6. Dias, C. J.; Das-Gupta, D. K. IEEE Trans Dielectric Electrical Insulation 1996, 3, 706.
7. Schwarzer, S.; Roosen, A. J Eur Ceram Soc 1999, 19, 1007.
8. Gregorio, R., Jr.; Cestari, M.; Bernardino, F. E. J Mater Sci 1996, 31, 2925.
9. Gregorio, R., Jr.; Ueno, E. M. J Mater Sci 1999, 34, 4489.
10. Satish, B.; Sredevi, K.; Vijaya, M. S. J Phys D: Appl Phys 2002, 35, 2048.
11. Venkatragavaraj, E.; Satish, B.; Vinod, P. R.; Vijaya, M. S. J Phys D: Appl Phys 2001, 34, 487.
12. Liu, Y.; Wang, X.; Zeng, X. J Phys IV France 2005, 126, 143.
13. Malmonge. L. F.; Malmonge, J. A.; Sakamoto. W. K. Mater Res 2003, 6, 469.
14. Abraham, T. Am Ceram Soc Bull 2000, 79, 45.
15. Abdullah, M. J.; Das-Gupta, D. K. IEEE Trans Dielectrics Electrical Insulation 1990, 3, 605.