

Enhanced Permittivity by the Adhesion of Conducting and Low-Loss Insulating Ceramics in Polystyrene

Sumesh George, Mailadil Thomas Sebastian

Materials and Minerals Division, National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695 019, India

Received 26 March 2008; accepted 25 August 2008

DOI 10.1002/app.30375

Published online 24 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: $\text{Ca}[(\text{Li}_{1/3}\text{Nb}_{2/3})_{0.8}\text{Ti}_{0.2}]\text{O}_{3-\delta}$ (CLNT)–polystyrene– $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (LSCO) three-phase composites were prepared by a two-step mixing and hot-molding method. The dielectric properties of polystyrene–CLNT composites were in agreement with the theoretical predictions. The dielectric properties of the three-phase composites were investigated in terms of the volume fraction of LSCO and the frequency. The relative permittivity of the composites increased with LSCO loading. These compo-

sites with low processing temperatures showed a maximum relative permittivity of the order of 10^4 . These composites, with a giant permittivity with a broad smearing region, can find application in electrostrictive, decoupling capacitors and embedded passive devices. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1682–1686, 2009

Key words: composites; dielectric properties; polystyrene

INTRODUCTION

Recently, significant efforts have focused on the development of high-relative-permittivity composites that are suitable for embedded passive devices and electrostrictive applications.¹ The majority of the electronic components in microelectronic circuits are passive and occupy more than 80% of the printed wired surface area.² The integration of passive components in printed circuit boards offers a significant reduction in size, improved electrical performance, and reliability. In the context of high-permittivity composites, several ceramic–metal,^{3–7} polymer–metal,^{8–12} and polymer–ceramic^{13–16} composites have been extensively studied. However, a high processing temperature limits the ceramic–metal composites in printed circuit board applications. Polymer-based composites provide an ideal solution by combining the dielectric properties of ceramic or metal with a polymer. These composites have a high relative permittivity, flexibility, compatibility, and low processing temperature and can be easily fabricated into various shapes. The commonly used ceramic fillers in polymer ceramic composites are ferroelectrics, which have high dielectric loss compared to low-loss dielectrics.^{17,18} Many of the ferroelectric ceramics are

lead based and are not environmentally friendly. It has been reported that high filler loadings in polymers are necessary to enhance the relative permittivity of polymer–ceramic composites.^{14–16} However, high filler loadings lead to poor flexibility and adhesion to the substrate.¹⁹ Three-phase composites consisting of a polymer, ceramic, and metal have attracted significant attention because of their high relative permittivity and low processing temperature.^{2,5,20–24} In this article, we report an enhancement in the relative permittivity of polymer-based three-phase composites by the adhesion of conducting and insulating ceramics. In these three-phase composites, $\text{Ca}[(\text{Li}_{1/3}\text{Nb}_{2/3})_{0.8}\text{Ti}_{0.2}]\text{O}_{3-\delta}$ (CLNT) was taken as the low-loss dielectric because it shows excellent microwave dielectric properties, [relative permittivity, $\epsilon_r = 38$, dielectric loss, $\tan d = 10^{-4}$, and temperature coefficient of relative permittivity, $\tau_\epsilon = 0$ ppm/°C at 4 GHz].²⁵ The crystalline $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (LSCO) has a high conductivity comparable to that of metals, and its use prevents the oxidation problem of metals.^{26,27} Hence, LSCO was used as the conducting phase for this composite. In percolative composites, the sharp increase in the relative permittivity near the percolation threshold is called the *smearing region*, in which isolated particles are shifted to interconnected clusters. Generally, all ceramic–metal and polymer–metal composites have very narrow smearing regions.^{3–7,9–12} It was reported that the addition of ceramic to polymer–metal composites isolates the metal particles from the clusters, which results in the expansion of the smearing region.²² As a result, more metal particles can be incorporated into the

Correspondence to: M. T. Sebastian (mailadils@yahoo.com).

Contract grant sponsor: Defence Research and Development Organization (New Delhi, India).

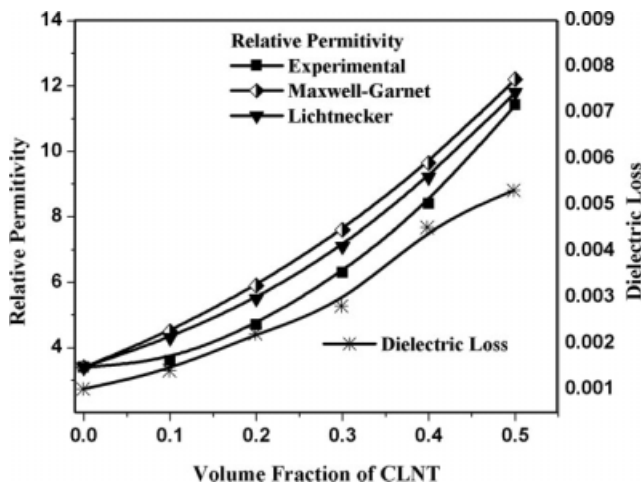


Figure 1 Variation of the relative permittivity and dielectric loss of CLNT-polystyrene composites at 1 MHz and comparison of the experimental relative permittivity with the theoretical model.

composites. The composite under study showed a broad smearing region, which improved the reproducibility and workability. These three-phase composites, with a giant permittivity, low processing temperature, and broad smearing region, can find application in embedded passive and electrostrictive devices.

EXPERIMENTAL

The CLNT-polystyrene-LSCO three-phase composites were prepared by a two-step mixing and hot-molding method. The low-loss CLNT and conducting LSCO were prepared by a solid-state ceramic route. Different volume fractions of sintered CLNT ceramics were melt-mixed with polystyrene with a sigma blade. We hot-molded these composites by pressing at about 150°C for 20 min under a pressure of 200 MPa. Polystyrene loaded with CLNT (a 0.40 volume fraction) was ground well to form a fine powder. Different volume fractions of LSCO were added to this fine powder and mixed for 1 h. The powder containing CLNT, polystyrene, and LSCO was hot-pressed at about 150°C for 20 min under a pressure of 200 MPa. Electrodes were connected to both sides of the disk-shaped composites with silver paste, and these samples were used to measure the dielectric properties. The dielectric properties were measured with an inductor capacitor resistor (LCR) meter (3532-50 LCR Hi Tester, Hioki, Japan). The microstructures of the sintered samples were studied with a scanning electron microscope (JSM 5600 LV, Jeol, Tokyo, Japan).

RESULTS AND DISCUSSION

Figure 1 shows the variation of the dielectric properties of the CLNT-polystyrene two-phase composites

with different volume fractions of CLNT loading. A gradual increase in the relative permittivity with CLNT loading was observed, which was due to the high relative permittivity of the CLNT ceramics compared to the polystyrene. At a high volume fraction of ceramic loading, the connectivity among the ceramic particle increased, which, in turn, increased the relative permittivity. Several groups have proposed numerical relations to predict the effective relative permittivity (ϵ_{eff}) of the polymer-ceramic composites.^{20,28,29} Figure 1 also compares the relative permittivity calculated with the Maxwell-Garnet relation [eq. (1)] and Lichtnecker relation [eq. (2)] with the experimental results:

$$\epsilon_{eff} = \epsilon_1 \left[1 + \left(\frac{3f\beta}{1-f\beta} \right) \right] \tag{1}$$

$$\ln \epsilon_{eff} = f \ln \epsilon_2 + (1-f) \ln \epsilon_1 \tag{2}$$

where

$$\beta = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} \tag{3}$$

where ϵ_2 is the relative permittivity of the CLNT ceramic at 1 MHz, ϵ_1 is the relative permittivity of polystyrene at 1 MHz, and f is the volume fraction of the CLNT ceramic. The experimental results were in agreement with the theoretical modeling. Higher ceramic loadings resulted in imperfect particle dispersion and limited the processability and flexibility. The composites with a 40% CLNT loading of polystyrene had a relative permittivity of 8.4 with $\tan \delta = 0.004$ at 1 MHz.

The relative permittivity of the polymer ceramic composites was enhanced further by the incorporation of a conducting phase in the two-phase composites. Hence, we added conducting LSCO ceramics as a third component in the polystyrene with a 0.40

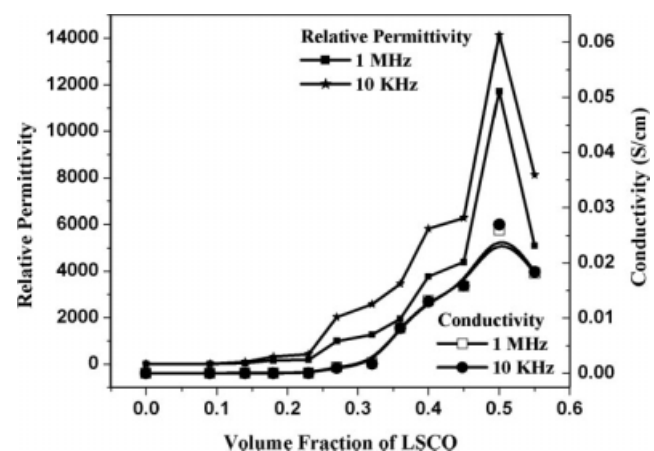


Figure 2 Variation of the relative permittivity and conductivity of CLNT-polystyrene-LSCO three-phase composites as a function of LSCO at 1 MHz and 10 kHz.

TABLE I
Dielectric Properties, Densities, and Conductivities of the CLNT–Polystyrene–LSCO Three-Phase Composites Measured at 1 MHz

Volume fraction of polystyrene	Volume fraction of CLNT	Volume fraction of LSCO	Experimental density (g/cm ³)	1 MHz		
				Relative permittivity	Tan δ	Conductivity (s/cm)
—	1.0	—	4.12	41	10 ⁻⁴	2.8 × 10 ⁻⁸
1.0	—	—	1.01	3.4	10 ⁻³	1.11 × 10 ⁻⁸
0.60	0.40	—	2.19	9.6	0.004	2.5 × 10 ⁻⁸
0.54	0.37	0.03	2.6	12.2	0.02	1.8 × 10 ⁻⁷
0.51	0.35	0.14	2.8	41.8	0.2	6.9 × 10 ⁻⁶
0.48	0.34	0.18	2.91	162.7	0.33	3.2 × 10 ⁻⁵
0.45	0.32	0.23	3.19	183	0.53	6.5 × 10 ⁻⁵
0.42	0.31	0.28	3.43	991	1.5	1 × 10 ⁻³
0.38	0.30	0.32	3.49	1273	1.8	2 × 10 ⁻³
0.35	0.29	0.36	3.50	1949	2.3	8.2 × 10 ⁻³
0.32	0.28	0.40	3.61	3768	3	1.45 × 10 ⁻²
0.28	0.27	0.45	3.63	4400	3.9	1.4 × 10 ⁻²
0.24	0.26	0.50	3.64	11713	3.6	2.6 × 10 ⁻²
0.20	0.25	0.55	3.645	5095	3.76	1.8 × 10 ⁻²

volume fraction of CLNT. Figure 2 shows the variation of the relative permittivity and conductivity of the CLNT–polystyrene–LSCO composites as a function of LSCO loading. The addition of LSCO increased the relative permittivity and conductivity of the composite. The increase in the relative permit-

tivity was a result of interfacial polarization, which occurs at the interface of dissimilar materials.³⁰ The charge carriers in the different phases of the composites were trapped at the interface within the dielectrics. These charges were unable to discharge freely and caused a rise in the overall field distortion. This

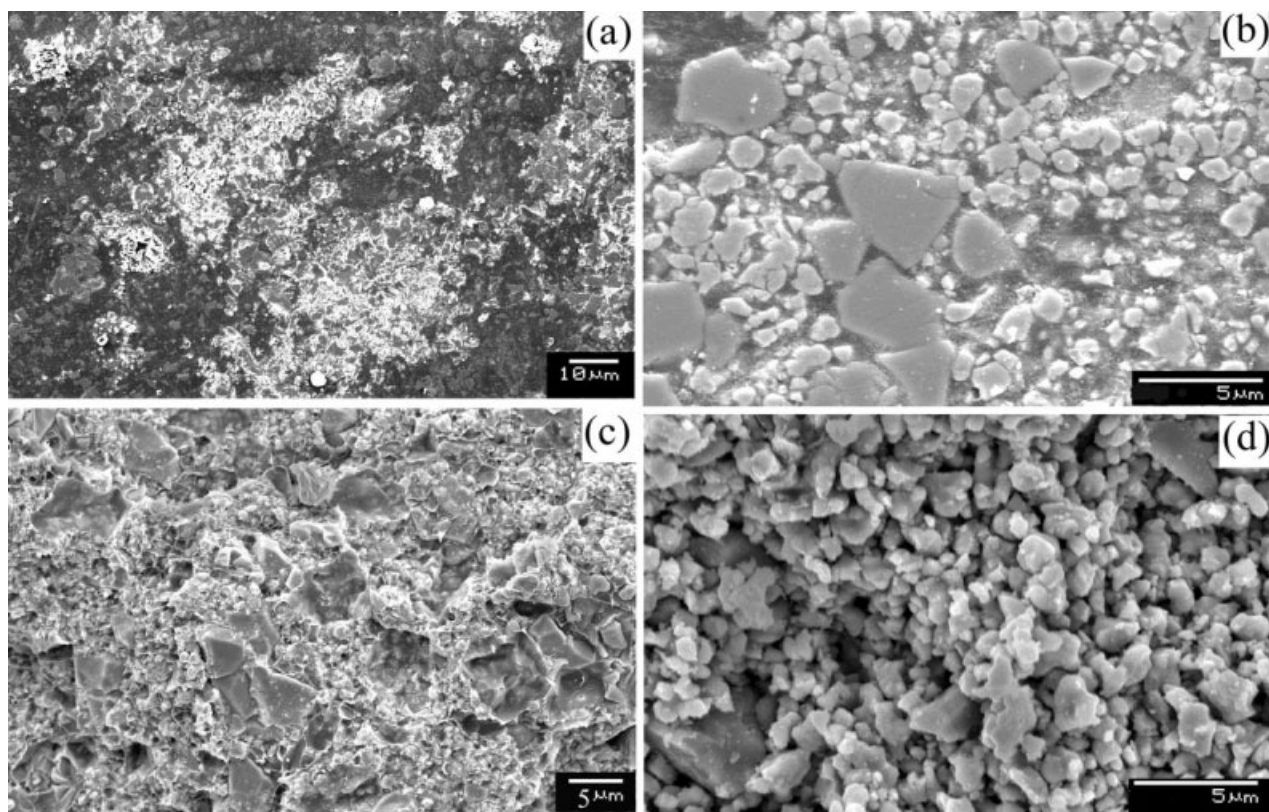


Figure 3 Microstructures of (a) polystyrene and CLNT (0.40 volume fraction), (b) an LSCO (0.40 volume fraction)-loaded polystyrene–CLNT composite, (c) the fractured surface of an LSCO (0.40 volume fraction)-loaded polystyrene–CLNT composite, and (d) the fractured surface of an LSCO (0.55 volume fraction)-loaded polystyrene–CLNT composite.

dielectric field³¹ that developed around the conducting phase resulted in an increase in the relative permittivity. The existence of a large number of conducting particles in parallel and blocked by thin insulating layers can also increase the relative permittivity.^{7,8} Each conducting phase in the composite acted as an internal electrode of tiny capacitors. These tiny supercapacitor networks with the large electrode area and small dielectric thickness macroscopically added up to result in a giant permittivity. The conductivity of this three-phase composite also increased with LSCO loading. As the volume fraction of LSCO increased, the cluster of LSCO merged, and there was a continuous path of the adjacent site across the system. Generally, all percolative composites have a small smearing region³⁻¹² ($V_c - V \approx 0.03$, where V and V_c are the volume fractions of the conducting filler below and at percolation, respectively). However, as shown in Figure 2, the relative permittivity increased from 183 to 11,713 with an increase of the volume fraction of LSCO from 0.23 to 0.50 in this three-phase composite. Hence, this system showed a broad smearing region ($V_c - V$) of 0.27 and had an improved reproducibility. As shown in Figure 2, the addition of more than a 0.50 volume fraction of LSCO decreased both the relative permittivity and conductivity of the three-phase composites. At higher volume fractions, the conducting phase agglomerated to form clusters and, thereby, increased the distance between the conducting particles.^{7,8} The poor dispersion of ceramics in the polymer matrix at higher ceramic loadings may have also decreased the relative permittivity. Hence, the relative permittivity and conductivity decreased in the three-phase composites for volume fractions of LSCO loading larger than 0.50.

Table I shows the volume fraction of each component in the three-phase composite and its physical and dielectric properties (1 MHz). The relative permittivity and dielectric loss increased with increasing volume fraction of LSCO. The increase in the dielectric loss with LSCO addition was due to its relatively high dielectric loss compared to CLNT and polystyrene. The addition of LSCO increased not only the permittivity but also $\tan \delta$. However, there are number of applications, such as flash lamps and heart actuators, working at low frequencies, for which a large capacitance is more important than the dielectric loss.²⁴ The bulk density increased with increasing LSCO loading. This was because of the relatively high density of LSCO (6.6325 g/cc) compared to CLNT and polystyrene. However, for a higher volume fraction of LSCO ceramic loading, the density did not increase proportionally. This was because of the poor adhesion of the ceramic in polystyrene,²⁹ which, in turn, degraded the dielectric properties at higher LSCO loadings in this three-phase composites.

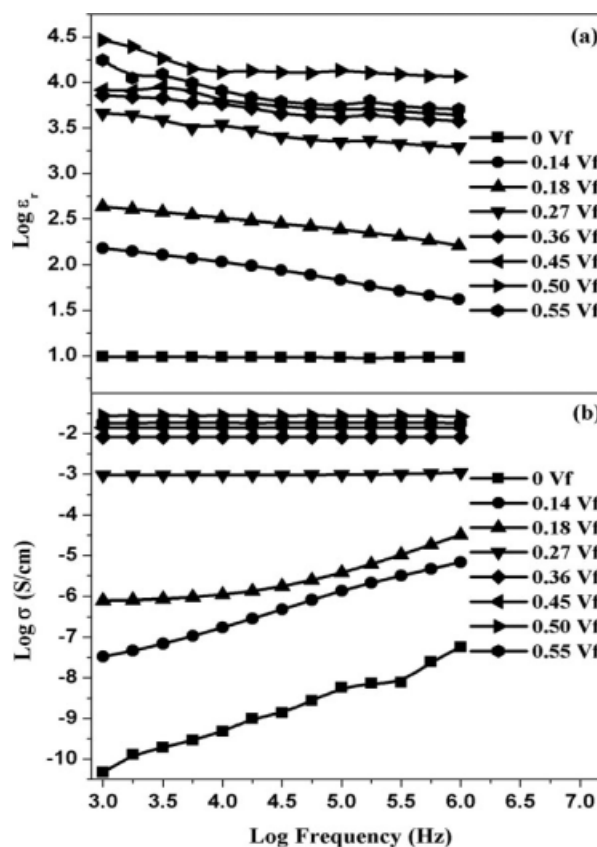


Figure 4 Variation of (a) the relative permittivity (ϵ_r) and (b) conductivity (σ) of CLNT-polystyrene-LSCO three-phase composites as a function of frequency (V_f = volume fraction).

Figure 3(a) shows the microstructure of a 0.40 volume fraction of a composite containing CLNT loading in the polystyrene. The ceramic particles were distributed randomly in the polymer matrix. The microstructure of a 0.40 volume fraction of an LSCO-loaded three-phase composite is shown in Figure 3(b). The large grains about 3–5 μm in size were LSCO, and the smaller grains were CLNT; they were randomly distributed in the polymer matrix. From the fractograph of a 0.40 volume fraction of the LSCO-loaded three-phase composite [see Fig. 3(c)], it was clear that the polystyrene acted as a good adhesive for combining LSCO and CLNT. However, a higher volume fraction of ceramic loading led to poor adhesion for combining the filler. Figure 3(d) shows the fractograph of a 0.55 volume fraction of an LSCO-loaded three-phase composite. We observed that a sufficient amount of polystyrene was not present in the composite to combine the ceramic particles, and this led to an increase in the porosity.

Figure 4 shows the frequency dependence of both the relative permittivity and conductivity of the CLNT-polystyrene-LSCO composite. A gradual decrease in the relative permittivity with frequency

was observed for all of the composites. This was expected because different polarization mechanisms are frequency dependent. It has been reported that the gradual decrease in permittivity with frequency was due to an interfacial relaxation.^{3,4,7-12} We observed that the conductivity increased with increasing frequency for a low volume fraction of LSCO loading. According to percolation theory, below the percolation threshold, the conductivity is proportional to the applied frequency (conductivity = f^x , where f is the frequency and x is a critical exponent).²⁸ The frequency dependence of relative permittivity and conductivity of disordered solids generally results from the polarization between the clusters and anomalous diffusion within each cluster. The capacitive effect between clusters on the conductivity and relative permittivity becomes significant at high frequency. As a result, the conductivity increases, and the relative permittivity decreases with frequency. Such a frequency-dependent behavior of this three-phase composite was in agreement with previous reports.⁷

CONCLUSIONS

CLNT-polystyrene-LSCO three-phase composites were prepared by a two-step mixing and hot-pressing method. The dielectric properties of the composites were investigated in terms of the volume fraction of LSCO and the frequency. The maximum relative permittivity ($\approx 10^4$) was observed for a 0.50 volume fraction of LSCO loading in the CLNT-polystyrene composites. The giant permittivity with the low processing temperature and broad smearing region of these three-phase composites will make them attractive materials for embedded passive applications.

References

- Chen, F.; Chu, C.; He, J.; Yang, Y.; Lin, J. *Appl Phys Lett* 2004, 85, 3295.
- Lu, J.; Moon, K. S.; Xu, J.; Wong, C. P. *J Mater Chem* 2006, 16, 1543.
- Pecharroman, C.; Moya, J. S. *Adv Mater* 2000, 12, 294.
- Pecharroman, C.; Betegon, F. E.; Bartolome, J. F.; Esteban, S. L.; Moya, J. S. *Adv Mater* 2001, 13, 1541.
- Choi, H. W.; Heo, Y. W.; Lee, J. H.; Kim, J. J.; Lee, H. Y.; Park, E. T.; Chung, Y. K. *Appl Phys Lett* 2006, 89, 132910.
- Xu, J.; Wong, C. P. *Appl Phys Lett* 2005, 87, 082907.
- George, S.; James, J.; Sebastian, M. T. *J Am Ceram Soc* 2007, 90, 3522.
- Deepa, K. S.; Sebastian, M. T.; James, J. *Appl Phys Lett* 2007, 91, 202904.
- Huang, C.; Zhang, Q. *Adv Funct Mater* 2004, 14, 501.
- Li, Y. J.; Xu, M.; Feng, J. Q.; Dang, Z. M. *Appl Phys Lett* 2006, 89, 072902.
- Li, J. Y.; Huang, C.; Zhang, Q. *Appl Phys Lett* 2004, 84, 3124.
- Tjong, S. C.; Liang, G. D.; Bao, S. P. *Scr Mater* 2007, 57, 461.
- Li, L.; Takahashi, A.; Hao, J.; Kikuchi, R.; Hayakawa, T.; Tsurumi, T. A.; Kakimoto, M. A. *IEEE Trans Comp Packaging Technol* 2005, 28, 754.
- Bhattacharaya, S. K.; Tummala, R. R. *J Mater Sci Mater Electr* 2000, 11, 253.
- Dang, Z. M.; Lin, Y. H.; Nan, C. W. *Adv Mater* 2003, 15, 1625.
- Rao, Y.; Wong, C. P. *IEEE Polytronic Conf* 2002, 196.
- Bai, Y.; Cheng, Z. Y.; Bharti, V.; Xu, H. S.; Zhang, Q. M. *Appl Phys Lett* 2000, 76, 3804.
- Furukawa, T.; Fujino, F.; Fukada, E. *J Appl Phys* 1979, 50, 4904.
- Xu, J.; Moon, K. S.; Tison, C.; Wong, C. P. *IEEE Trans Adv Packaging* 2006, 29, 295.
- Dang, Z. M.; Shen, Y.; Nan, C. W. *Appl Phys Lett* 2002, 81, 4814.
- Li, B. W.; Shen, Y.; Yue, Z. X.; Nan, C. W. *J Appl Phys* 2006, 99, 123909.
- Lim, E. S.; Lee, J. C.; Kim, J. J.; Park, E. T.; Chung, Y. K.; Lee, H. Y. *Integrated Ferroelectr* 2005, 74, 53.
- Prakash, B. S.; Varma, K. B. R. *Compos Sci Technol* 2007, 67, 2363.
- Lai, Q.; Lee, B. I.; Samuels, W. D.; Exarhos, G. J.; Parler, S. G. *J Polym Sci* 2006, 102, 967.
- Choi, J. W.; Kang, C. Y.; Yoon, J. W.; Kim, H. J.; Jung, H. J. *J Mater Res* 1999, 14, 3567.
- Ohabayashi, H.; Kudo, T.; Gejo, T. *Jpn J Appl Phys* 1974, 13, 1.
- Chainani, A.; Mathew, M.; Sarma, D. D. *Phys Rev B* 1992, 46, 9976.
- Nan, C. W. *Prog Mater Sci* 1993, 37, 1.
- Subodh, G.; Pavithran, C.; Mohanan, P.; Sebastian, M. T. *J Eur Ceram Soc* 2007, 27, 3039.
- Foulger, S. H. *J Polym Sci Part B: Polym Phys* 1999, 37, 1899.
- Chylek, P.; Srivastava, V. *Phys Rev B* 1984, 30, 1008.