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# High-K and Low Loss $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$/Polyimide Composite Films for Application in Embedded Capacitors

*Seung-Hoon Choi,*[1,2] *Il-Doo Kim,**[1] *Jae-Min Hong,*[1] *Seong-Guen Oh*[2]

**Summary:** We report on the role of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) ceramic fillers in notably reducing the dielectric loss of BZN/polyimide composite films manufactured for application in flexible RF embedded capacitors. The composite films were synthesized using a colloidal process. INAAT (isopropyl tris(N-amino-ethyl aminoethyl)titanate) was used as a coupling agent for homogeneous dispersion of BZN particles into a polyimide matrix. The BZN/polyimide composite films (BZN content at 50 Vol%) exhibited a low dielectric loss of 0.0369 at 12 MHz while retaining a high dielectric constant of 14.75.

**Keywords:** BZN; capacitors; dielectric properties; embedded; polyimides

## Introduction

Flexible embedded-capacitors are important emerging elements that can provide significant improvement in the performance and functionality of plastic-based electronic devices. They can also offer reduced inductance by decreasing the length of interconnects.[1–2] In particular, composite films based on polymer/high-K ceramic fillers have been widely studied in efforts to combine the flexibility of organic polymers with the enhanced dielectric properties of high-K ceramic fillers. Ferroelectric materials such as $BaTiO_3$, $Pb(Zr,Ti)O_3$, and $Pb(Mg,Nb)O_3$-$PbTiO_3$ have been extensively employed as high-K ceramic fillers due to their intrinsic features which induce a high dielectric constant in composite films.[3–4] The dielectric properties of polymer/ceramic composite films are largely influenced by the dispersion and loading of the ceramic in the polymer matrix. In order to increase the effective dielectric constant of polymer/ceramic composite films, larger loading volume with homogeneous dispersion of ceramic fillers is important. However, composite films comprised of ferroelectric fillers with high volume content generally suffer from high dielectric losses in the microwave frequency region due to the intrinsic capacitive hysteresis of ferroelectric materials.[5] Therefore, new ceramic fillers with low losses that can still retain a high dielectric constant at a high frequency regime are required.

The $Bi_2O_3$–ZnO–$Nb_2O_5$ (BZN) system has been studied intensively over the past few years as a promising dielectric material for use in low-fire multilayer ceramic capacitors and microwave tunable devices such as tunable filters and phase shifters.[6] Paraelectric $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ has a pyrochlore structure and is known to have high dielectric constants in a range of 170–220 with a low dielectric loss tangent ($5 \times 10^{-4}$) and high resistivity ($3 \times 10^{13}$ Ωcm).[6] More recently, room temperature processed BZN films with high-K values were characterized for applications in low voltage operating thin film transistors as gate insulators and thin film embedded capacitors.[7–8] However, few articles have been

[1] Optoelectronic Materials Research Center, Korea Institute of Science and Technology, P.O. Box 131 Cheongryang, Seoul 130-650, Republic of Korea
Fax: (+82) 02 958 5309
E-mail: idkim@kist.re.kr
[2] Department of Chemical Engineering, Hanyang University, Haengdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea

published on composite films using pyrochlore structured BZN as a high-K ceramic filler for use in flexible embedded capacitors. In this study, we use polyimide as an organic polymer due to its reliable high temperature stability, good mechanical strength, and excellent chemical stability. Polyimide/BZN (1.3 μm) composites were prepared by condensation polymerization of dianhydride and diamine with surface reformed BZN particles in N,N′-dimethylacetamide(DMAc), followed by thermal imidization. We report on the effects of a new ceramic filler, e.g. $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$, in terms of achieving a high dielectric constant and low dielectric loss in polyimide/BZN composite films. The reduction in dielectric loss of polyimide/BZN composite films as compared to that of polyimide/$BaTiO_3$ composite films is also discussed.

### Materials and Preparation of Polyimide/BZN Composite Films

BZN ceramic fillers were prepared by a conventional mixed oxide method. For homogeneous dispersion of BZN ceramic fillers, we used a coupling agent of isopropyl tris(N-amino-ethyl aminoethyl)-titanate (INAAT) with three organic moieties. INAAT of 1.6 g was dissolved in a water (100 ml) and BZN particles (40.0 g) were added into a flask. The mixtures were ultrasonicated at room temperature for 10 min. and stirred mechanically at 70 °C for 1 hr. and then centrifuged. The obtained BZN was subsequently washed by ethanol and dried in a vacuum oven at a temperature of 50 °C in order to remove residual solvent. Finally, INAAT modified BZN particles were obtained.

The polyimide (PI) precursor poly(amiic acid) (PAA) was prepared by in situ polymerization of PMDA (pyromellitic dianhydride) and ODA (4,4'-oxydianiline) in DMAc (N,N-dimethlyacetamide) solvent. The INAAT treated BZN fillers were mixed in PAA solution. The homogeneous suspension was spread on a clean, dust-free glass plate using a doctor blade. The solvent was then removed in a desiccator at room temperature using a low vacuum pump. Finally, the PAA/BZN composite films with a thickness of 40 ± 3 μm were baked for imidization at a temperature of 300 °C for 1 hr.

The structural properties of the composite films were characterized by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). X-ray diffraction analysis was used to identify the phases. The microstructure and roughness of the polyimide/BZN composite films were investigated by scanning electron microscopy (SEM). For electrical measurements, Au electrodes (Area = 0.5 $cm^2$) of 100 nm thickness were deposited through a shadow mask on the polyimide/BZN composite films by dc magnetron sputtering. The dielectric properties were measured in a frequency range from 10 kHz to 12 MHz with an applied electric field up to 30 V using an HP4192A impedance analyzer.

## Results and Discussion

Figure 1 shows the FT-IR spectra of (a) pure polyimide film, (b) BZN/polyimide composite film, (c) untreated BZN, and (d) INAAT treated BZN particles, respectively.

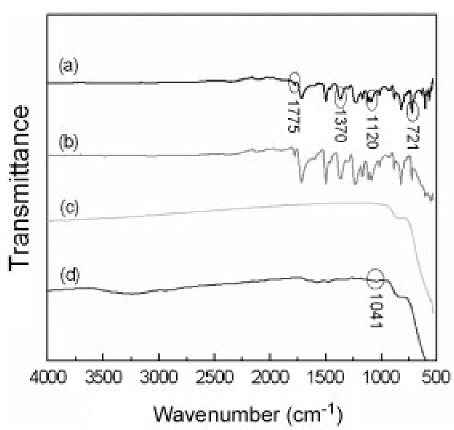


*Figure 1.*
FT-IR spectra of (a) pure polyimide, (b) polyimide/INAAT modified $BaTiO_3$ composite films, (c) untreated BZN particles, and (d) INAAT-modified BZN particles.

 

As shown in Figure 1(d), INAAT modified BZN particles exhibited new absorption bands at a wave number of 1041 $cm^{-1}$, which is the characteristic peak of the Ti–O–Ti unit from the INAAT coupling agent. On the other hand, the characteristic peak of the Ti–O–Ti unit was not observed in untreated BZN particles. These results indicate that the coupling agent of INAAT reacted effectively with the surface of the BZN particles. In addition, the characteristic polyimide peaks are clearly observed at wave numbers of 1775, 1370, 1120, and 721 $cm^{-1}$.[9] Since the FT-IR spectrum for the polyimide/BZN composite films ranged from 600 to 4000 $cm^{-1}$, the absorption of BZN between 500 to 600 $cm^{-1}$ could not be characterized. However, the absorption bands of BZN above 500 $cm^{-1}$ are thought to be mostly related with O-(ZnNb)-O bending modes.[10] Further study is needed to investigate the absorption bands of BZN particles in polyimide/BZN composite films.

In order to investigate the crystallinity and the structure of the polyimide/BZN composites, an X-ray diffraction pattern analysis was conducted. Figure 2 shows the XRD patterns of the polyimide/BZN composite as a function of BZN content. The XRD analysis for the polyimide revealed a phase pure amorphous structure, which is associated with the broad peak of $2\theta$ centered around 18° (data not shown).

The polyimide/BZN composite film with various BZN content reflected the typical cubic pyrochlore structure of BZN ceramic fillers, characterized by (111), (222), (400), and (622) peaks. Undesired secondary phases were not observed in the polyimide/BZN composite films. As shown in Figure 2, the intensities of diffraction peaks were slightly increased with an increase of BZN content in the composite films. The BZN material that is used as a ceramic filler in composite films has a cubic pyrochlore structure with the general formula unit $A_2B_2O_6O'$, where O′ is the seventh oxygen bonded only to the A site. The relatively large A cation is in an eightfold coordination, with oxygen anions, while the smaller

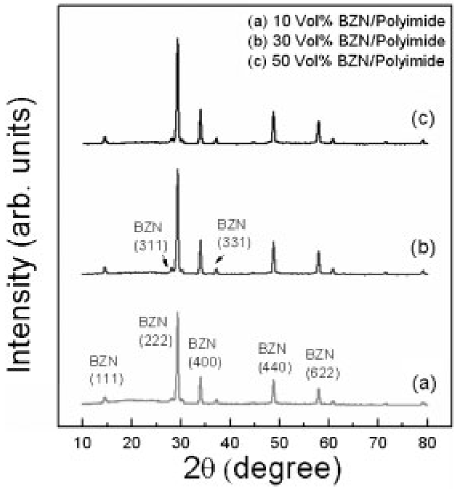


***Figure 2.***
X-ray diffraction patterns of polyimide/INAAT modified BZN composite with the content of BZN volume fraction.

B cation resides in a sixfold coordination forming a ($BO_6$) oxygen octahedra.[11] In general, the bulk Bi pyrochlores have a low sintering temperature, below 950 °C, as compared to that (1300 °C) of perovskite phase such as $BaTiO_3$, $Pb(Zr,Ti)O_3$, etc.[12]

Recently, $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ ceramics were synthesized by a metallo-organic decomposition (MOD) route at temperatures ranging from 500 to 700 °C.[13] Low processing temperature for the preparation of a ceramic filler is attractive in that it offers a simple and cost-effective manufacturing process.

Figure 3 shows the surface morphologies of polyimide/BZN composite films. The polyimide/INAAT-treated BZN composite films (BZN contents from 10 to 50 vol%) showed greatly enhanced distribution throughout the entire polyimide matrix. They appear homogeneous and smooth. These results are associated with the enhanced homogeneous dispersion obtained as a result of using the INAAT coupling agent with three organic moieties. A large number of organo functional groups (organic moiety) on the BZN surface can enhance inorganic/organic phase compatibilization at the interface, thereby increasing the

 

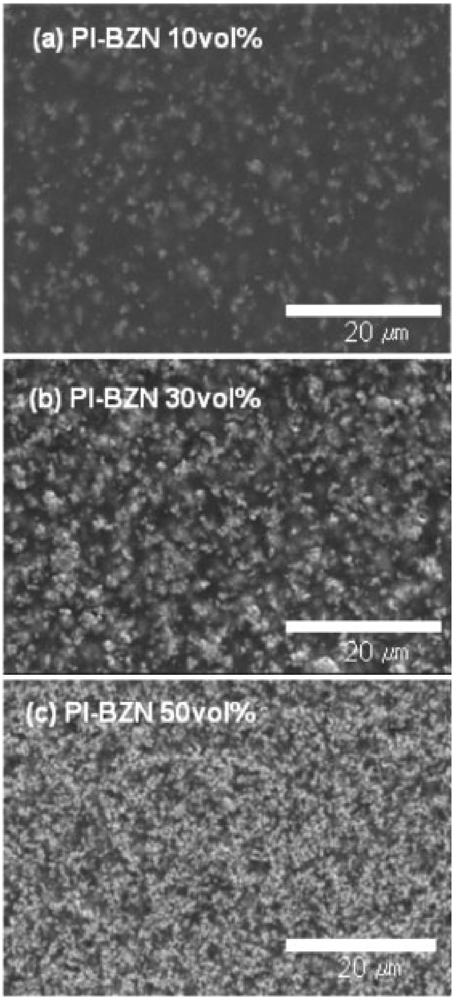


***Figure 3.***
SEM micrographs of the polyimide/INAAT-modified BZN composite films with BZN content of 10, 30, 50%, respectively.

degree of dispersability in the polymer matrix.[14] Thus, good dispersion of the BZN ceramic fillers can induce homogeneous packing, leading to uniformity of properties and a higher dielectric constant.

In order to investigate the dielectric properties of polyimide/BZN composite films, capacitors with a MIM (metal-insulator-metal) configuration of Au/composite/Au were fabricated. We measured the frequency dependent-dielectric properties of the composite films with a HP4192A impedance analyzer and calculated the dielectric constant from the capacitance values using the parallel-plate formula and the film thickness.

Figure 4 shows the measured dielectric constant and dielectric loss of the polyimide composite films filled with 1.3 μm BZN particles treated by INAAT coupling agent as a function of the BZN volume fraction. The relative volume % of BZN filler to polyimide was varied from 10 to 50. The dielectric constant of the polyimide/BZN composite films increased with an increase of the volume fraction of BZN particles, as shown in Figure 4(a). The loss factor slightly decreased from 0.0065 to 0.0052 at 1 MHz as the BZN fraction increased from 10 to 50 vol%. These results reveal that the BZN particles serve to increase the dielectric constant while retaining excellent dielectric loss properties. As shown in Figures 4(a), the polyimide/INAAT-treated BZN composite had a higher dielectric constant ($\varepsilon_r = 14.72$) compared to that of the polyimide film ($\varepsilon_r = 3.3$). The composite exhibited no significant frequency dependence from 10 kHz to 1 MHz. The low-frequency dependence of the dielectric constant and dielectric loss ensures more predictable operation of embedded capacitors.

Figure 4(b) shows the higher frequency dependence from 1 MHz to 12 MHz for the dielectric constant and dielectric loss of the polyimide/INAAT-treated BZN composite films. The composite films exhibited slight frequency dependence with small variation of dielectric loss from 1 MHz to 12 MHz. The overall changes in the loss tangent were less than 4% at a frequency of 12 MHz. The low dielectric loss may be ascribed to the unique structural behaviors of BZN particles. In BZN, Bi and Zn are randomly mixed on the A site of the pyrochlore structure ($A_2B_2O_6O'$). Both the A cations and O′ ions are randomly displaced from their ideal positions in the cubic pyrochlore. The movement of these off-centered ions is thought to contribute to the relatively broad dielectric relaxation in BZN.[15] Indeed, the dielectric loss of polyimide/BZN

 

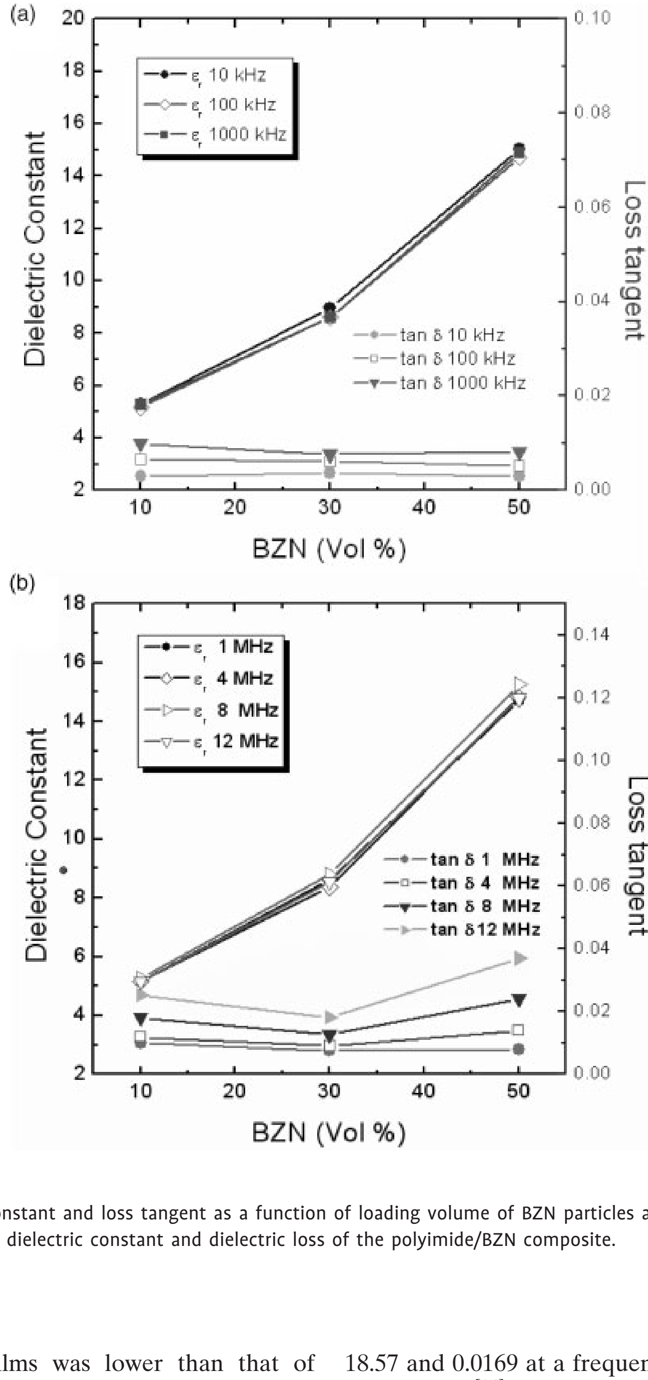


***Figure 4.***
(a) Dielectric constant and loss tangent as a function of loading volume of BZN particles and (b) frequency dependence for dielectric constant and dielectric loss of the polyimide/BZN composite.

composite films was lower than that of polyimide/$BaTiO_3$ composite films at a frequency of 12 MHz. In particular, in the case of polyimide/$BaTiO_3$ composite films containing 50 vol% of $BaTiO_3$ (particle size : 70 nm, tetragonal ferroelectric phase), the dielectric constant and dielectric loss were 18.57 and 0.0169 at a frequency of 1 MHz, respectively.[14] On the other hand, polyimide/BZN composite films exhibited a comparable dielectric constant of 14.72 and significantly improved dielectric loss of 0.0052 due to the low dielectric loss characteristics of the BZN fillers.

## Conclusion

In summary, high dielectric constant and low dielectric loss polyimide/BZN composite films were prepared using pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline-(ODA)-based polyimide. Homogeneous dispersion of pyrochlore structure BZN particles was obtained by the use of an isopropyl tris(N-amino-ethyl aminoethyl)-titanate (INAAT) coupling agent. The polyimide composite with BZN particles (BZN content at 50 vol%) treated by INAAT showed a reduced dielectric loss of 0.0369 at 12 MHz while retaining an appropriate dielectric constant of 14.75. These results demonstrate the potential of employing BZN ceramic fillers for obtaining reduced dielectric loss while retaining a relatively high dielectric constant in a polyimide/BZN composite for application in a RF embedded capacitor in the microwave frequency regime.

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