Effective dielectric properties of Cement/ Ba$_{0.06}$(Na$_{0.5}$Bi$_{0.5}$)$_{0.94}$TiO$_3$ composites: A comparative approach

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Abstract. Lead-free ceramic powder of a morphotropic phase boundary composition Ba$_{0.06}$(Na$_{0.5}$Bi$_{0.5}$)$_{0.94}$TiO$_3$ (BNBT) was prepared from a solid-state synthesis route. The cement-ceramic (1-$\phi$)cement/$\phi$BNBT; 0 $\leq$ $\phi$ 1.0 composites were fabricated. The filler concentration-dependent values of the bulk density and real part of complex permittivity showed an increasing trend of variation while the apparent porosity and imaginary part of complex permittivity followed a decreasing trend. In order to test the acceptability of dielectric mixture equations of the inclusion material in the mixture, five such equations have been chosen. The Bruggeman, and Rother-Lichtennecker equations showed their coherence with minimal deviation from the experimental results of the real part of complex permittivity for the entire measurement range of volume fractions. Also, a first-order exponential growth/decay type of mathematical model was suggested which could fit the experimental data excellently well ($r^2 > 0.97$).

1. Introduction

In recent years, cement-based piezoelectric composites have gained much attention due to their smart transduction properties and better compatibilities with the most common construction materials used in civil engineering, especially in non-destructive real-time in-situ structural health monitoring applications [1-7]. The 0-3 type cement-based composites have become popular among the 0-3, 1-3, and 2-2 connectivity composites because they contain zero-dimensioned piezoelectric ceramic particles in the cement matrix connected in three dimensions and are easy to fabricate and capable of mass production. Also, the properties of such composites can effectively be tailored by varying the composition. Moreover, the issue of deciding the actual dielectric properties of such composites has been the subject of echoed worldwide concern in recent years [8-10].

Further, the MPB composition of ABO$_3$--type ferroelectric ceramic Ba$_{0.06}$(Na$_{0.5}$Bi$_{0.5}$)$_{0.94}$TiO$_3$ (BNBT) is recognized as a well-known lead-free option because it displays improved dielectric and piezoelectric properties. In this work, BNBT ceramic powder was mixed with Portland cement to form 0–3 cement/Ba$_{0.06}$(Na$_{0.5}$Bi$_{0.5}$)$_{0.94}$TiO$_3$ (abbreviated hereafter as Ce/BNBT) composites and investigated their density, apparent porosity, and dielectric properties. Also, studies for the estimation of the actual
dielectric constant as well as loss factor of the present composite system have been undertaken using different dielectric mixture equations.

2. Experimental
The synthesis of BNBT ceramic was made from AR-grade Alfa Assar chemicals (BaCO₃, Na₂CO₃, Bi₂O₃, and TiO₂; purity: excess of 99.9%). A solid-state synthesis procedure was adopted for this purpose, keeping the calcination temperature of 1140°C for four hours in the air atmosphere under controlled heating and cooling cycles according to the thermochemical reaction: 0.06BaCO₃ + \( \frac{2}{3} \) Na₂CO₃ + \( \frac{2}{3} \) Bi₂O₃ + TiO₂ → Ba₀.₈₆(Na₀.₃Bi₀.₄)₀.₉₄TiO₃ + 0.295CO₂(g). The completeness of the reaction and the creation of the soughed compound was confirmed by the X-ray diffraction (XRD) method. Thereafter, Pozzolana Portland cement (Jaypee group, India) and BNBT powder were blended with agate-mortar and pestle. The Water-Ce/BNBT powder proportion was utilized to fabricate the cylindrical pellets (diameter = 12 mm and thickness ~1.2 mm) for different characterizations, such as bulk density, apparent porosity, and dielectric properties. The Ce/BNBT composite samples were then kept in an open environment for one day. Thereafter, the samples were demoulded and cured by pouring them into a water pond for twenty-eight days. The bulk density (\( \rho_{cal} \)) of BNBT ceramic and cement (as per the IS code 4031 part 11) were taken as 5.0337 g/cm³ and 3.15 g/cm³ respectively. Besides, the theoretical density was estimated using the formula: \( \rho_{cal} = \frac{\phi_f \rho_f + (1-\phi_f)\rho_m}{m_f / [m_f + m_m(\rho_f / \rho_m)]} \); here, \( V_f \), \( V_m \), \( m_f \), \( m_m \) and \( \rho_f, \rho_m \) are the volume, mass and density of BNBT ceramic powder as filler and cement as a matrix respectively. The as-prepared Ce/BNBT paste was maintained at 0.33 in order to form a cement-BNBT paste. The values of volume fractions of BNBT powder were blended with agate-mortar and pestle. The Water-Ce/BNBT powder proportion was maintained at 80ºC/3h to remove moisture from the outer surface and air-dried silver paste was applied on both the flat faces of the pellets to measure the dielectric properties. The dielectric measurements at room temperature were accomplished using a HIOKI 3532-50 Japan makes LCR Hi-Tester interfaced with a personal computer.

3. Theoretical
The decisive estimation of the filler-concentration-dependent effective dielectric constant (\( \varepsilon_r' \)) and loss factor (\( \varepsilon_r'' \)) of composites is of much interest as far as the design of materials is concerned. The anticipating models as suggested by Furukawa, Knott, Bruggeman, Cuming, Taylor, Rother-Lichtenecker, Maxwell-Wagner, Hashin-Shtrikman, Poon-Shin, Wiener, Skipetrov, Lewin, modified Cule-Torquato, Sillars, Jayasundere-Smith, etc. were utilized to approximate \( \varepsilon_r' \) for a variety of composites [8-10]. However, the predictive models used as part of this study are described below.

(i) The equation given by Bruggeman (BE) is expressed as:

\[
\varepsilon_r' = \varepsilon_r''\left[1 + \frac{\phi_f (\varepsilon_r' - \varepsilon_r'')}{\varepsilon_r'' + (1-\phi_f) (\varepsilon_r' - \varepsilon_r'')}\right]^{1/(1-n)}
\]

where ‘f’ and ‘m’ as subscripts respectively, symbolize ‘filler’ and ‘matrix’. Here, ‘n’ is shape-dependent parameter and can be adjusted as per the need (data variation).

(ii) The equation given by Furukawa (FE) or Webman or Effective Medium Theory (EMT) is expressed as:

\[
\varepsilon_r' = \varepsilon_r''\left[1 + \frac{2\phi_f (\varepsilon_r' - \varepsilon_r'')/((\varepsilon_r' + 2\varepsilon_r''))}{1 - \phi_f (\varepsilon_r' - \varepsilon_r'')/((\varepsilon_r' + 2\varepsilon_r''))}\right]
\]
(iii) The equation proposed by Rother-Lichtenecker (RLE) or Cuming is given as:

\[ \varepsilon'_{\text{eff}} = \exp(\sum \phi_i \ln \varepsilon'_i) \]  

(3)

Here \( \phi_i \) and \( \varepsilon'_i \) are the volume fraction and dielectric constant respectively for the \( i^{th} \)-component of the composite.

(iv) If the shape-dependent parameter ‘\( k \)’ will be introduced in eqn. (3), the above equation could be expressed as modified RLE (mRLE):

\[ \varepsilon'_{\text{eff}} = \exp[\ln \varepsilon'_{\text{m}} + \phi (1-k) \ln(\varepsilon'_f / \varepsilon'_{\text{m}})] \]  

(4)

Equations (3) and (4) are regarded as the normal depictions of the logarithmic law of mixing for a statistical and/or chaotic mixture.

(v) The Knott equation (KE) is expressed as:

\[ \varepsilon'_{\text{eff}} = \varepsilon'_f \left[ 1 - \frac{(1 - \phi_f)(\varepsilon'_f - \varepsilon'_m)}{\varepsilon'_m + (1 - \phi_f)(\varepsilon'_f - \varepsilon'_m)} \right] \]  

(5)

The equations determining the filler-concentration reliant variation of \( \varepsilon'_{\text{eff}} \) for the composite materials, like that of \( \varepsilon'_f \), are very few in number. However, a formula provided by Bruggeman [11] states:

\[ \varepsilon'_{\text{eff}} = \frac{\varepsilon'_m[(\varepsilon'_f - \varepsilon'_m)(\varepsilon'_f + 2\varepsilon'_m)\varepsilon'_f]}{[(\varepsilon'_f - \varepsilon'_m)(\varepsilon'_f + 2\varepsilon'_m)] + \varepsilon'_f \frac{3(\varepsilon'_f - \varepsilon'_m)\varepsilon'}{(\varepsilon'_f - \varepsilon'_m)(\varepsilon'_f + 2\varepsilon')} \]  

(6)

In addition, this equation provides an alternative of utilizing all available models for \( \varepsilon'_{\text{eff}} \) to be used in eqn. (6) in order to find the respective \( \varepsilon'_{\text{eff}} \) values toward a comparison with experimental findings. Consequently, the equations (1-5) were assessed to predict the \( \varepsilon'_{\text{eff}} \) values of the Ce/BNBT 0-3 composites to be compared with the experimental findings.

4. Results and Discussion

The filler-concentration-dependent variation of \( \rho_{\text{exp}} \) and \( P(\%) \) of twenty-eight days’ water-cured Ce/BNBT composite sample at room temperature is depicted in Figure 1. The value of \( \rho_{\text{exp}} \) was found to increase from 2.66 to 4.93 g/cm\(^3\), while that of \( P(\%) \) decreased from 15.56 to 2.06 with the increasing BNBT-content. In addition, the value of \( \rho_{\text{exp}} \) (represented by a symbol) always remains a little lower compared to \( \rho_{\text{cal}} \) (represented by a line). This could be due to the creation of C-S-H gels on account of the hydration of cement and the existence of intermolecular-forces that occur between gel-to-gel bonding through the hydrogen bonding, O–Ca–O bridges, or condensation of Si(OH)\( _x \)-groups leading to the siloxane (Si–O–Si) linkages [1-3,12]. The siloxane-bonding is assumed to break with the inclusion of BNBT ceramic powder into the cement-matrix due to their interaction with siloxane [1-3,13], resulting in the Ti–O bonds of BNBT being connected with Si–O through the connecting oxygen that led to the development of Ti–O-….Si–O bonds. Besides, most of the BNBT particles do not take part in the chemical reactions with cement-matrix and stay intact in their original state. Likewise, an increase in the BNBT-content led to the growing diffusion of Ti-ions in the cement matrix. It reduces the vacant pores in Ce/BNBT composites, which decreases the porosity and consequently raises the bulk density. This result agrees well with the findings of similar cement-based composite systems [1-3].

Figures 2 and 3, respectively exhibit the variation of \( \varepsilon' \) and \( \varepsilon'' \) with the BNBT-content of Ce/BNBT composites (symbols: experimental data) along with the fitted curves for \( \varepsilon'_{\text{eff}} \) and \( \varepsilon''_{\text{eff}} \) provided by different test equations. It is observed that the value of \( \varepsilon' \) increases from 27 to 1150 while that of \( \varepsilon'' \) decreases from 53.46 to 41.4 by incrementing BNBT-content in the cement matrix. Further, the trends of variation of predictive models, BE and RLE, successfully demonstrate their agreement with the experimental results of the real part of dielectric constant for the whole range of \( \phi_f \). The excellent fitting
of \( \varepsilon' - \phi_f \) data by BE might be due to the adjustable parameter \((n)\), which comes to be 0.5 in the present case. In addition, other predictive equations such as FE and KE portray the insufficiency of explaining the \( \varepsilon' - \phi_f \) data, especially near to extreme ends. Further, it is seen that no predictive equations could fit the \( \varepsilon'' - \phi_f \) data.

It is seen that none of the mixture equations fit the experimental data of real and imaginary parts of the dielectric constant of Ce/BNBT composites except BE and RLE, which fitted the \( \varepsilon' - \phi_f \) data only. With the aim of finding an acceptable solution to the problem, a model for the filler (BNBT) content-dependent variation of real and imaginary parts of dielectric constant was proposed [9,14,15], which was applied to the present composite system through the curve-fitting method. Accordingly, a mathematical model (1\textsuperscript{st} order exponential growth/decay type) of the form [9,14,15]:

\[
Y = Y_o + A \exp(\pm \phi_f / t) = Y_o + A \exp(\pm \beta \phi_f)
\]  

was taken into consideration. The values of model parameters \(Y_o, A, t\), or \(\beta (=1/t)\) along with \(r^2\) for both real and imaginary parts of dielectric constant as obtained from curve-fitting have been detailed in Table 1, which exhibits that \(r^2 \rightarrow 1\) for both the parameters. Here, the term \((Y_o + A)\) is similar to the value of the real or imaginary part of the dielectric constant depending on the variation chosen. Also, \(\beta\) could be
reckoned as the filler concentration-dependent real or imaginary part of the dielectric constant growth/decay parameter. Figure 4 displays the dependence of real and imaginary parts of the dielectric constant on the volume fractions of Ce/BNBT composites, including the fitted curves (Eq. 7). The experimental data fit very well ($r^2 > 0.97$) with this theoretical model. Nonetheless, it arises from the present study that the value of $\beta$ assumes different values for different combinations of ceramic and cement. It could be due to offbeat densification characters of the cement-ceramic composites with increased volume fractions, where denser ceramic particles replace the lighter cement particles. Also, the increase in $\beta$ may be attributed to the proportion of the permittivity of ceramic-to-cement particles. So, the B values of such composites will surely deliver some idea of the nature (flat or sharp) of variation. It might be considered as a calibration parameter and thus believed to be advantageous for future study.

Table 1. List of fitted parameters for Eq. (7) applied on the real and imaginary parts of the dielectric constant data of 0-3 Ce/BNBT composites at room temperature and 1 kHz.

| Equations → Parameters ↓ | Exponential Growth/Decay: $Y = Y_o + A \exp(\pm \phi / t)$ | $Y_o$ | $A$ | $t$ | $r^2$ |
|-------------------------|-------------------------------------------------|-------|-----|-----|-------|
| $\varepsilon'$, Ce/BNBT | 6.87712                                        | 22.17917 | 0.25365 | 0.99996 |
| $\varepsilon''$, Ce/BNBT | 41.04037                                       | 12.79406 | 0.09713 | 0.97478 |

5. Conclusion
Lead-free ceramic powder $\text{Ba}_{0.06}(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.94}\text{TiO}_3$, prepared from a solid-state synthesis route was used to fabricate the $(1-\phi)$cement/$\phi$BNBT; $0 \leq \phi \leq 1.0$ composites. The filler concentration-dependent values of the bulk density and real part of dielectric constant followed an increasing trend of variation while that of apparent porosity and imaginary part of dielectric constant pursued a decreasing trend. With the aim of testing the acceptability of dielectric mixture equations of the inclusion material in the mixture, five equations were considered. The Bruggeman, and Rother-Lichtenecker equations showed their coherence with minimal deviation from the experimental findings of the real part of dielectric constant for the complete range of volume fractions. Besides, a mathematical model ($1^{st}$ order exponential growth/decay type) was suggested which could fit the experimental dielectric data excellently well ($r^2 > 0.97$).

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