MATERIAL COMPOZIT FORMAT DIN CERAMICĂ BINAR STRUCTURATĂ DE TIP PEROVSKIT – BRONZ DE WOLFRAM (0.5 PLZT – 0.5 PBBN) ŞI CIMENT PENTRU APLICAȚII DE MONITORIZARE STRUCTURALĂ ÎN CONSTRUCȚII

BINARY STRUCTURED PEROVSKITE-TUNGSTEN BRONZE 0.5PLZT-0.5PBBN CERAMIC DISPERSED CEMENT COMPOSITE FOR STRUCTURAL HEALTH MONITORING APPLICATIONS

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A unique binary structured perovskite (Lead Lanthanum Zirconium Titante: PLZT) and tungsten bronze (Lead Barium Bismuth Niobate: PBBiN) piezoelectric material with Ordinary Portland Cement: OPC composites were fabricated by solid state reaction method. The composites were fabricated with ceramic to cement in the ratios of 25:75vol%, 50:50vol% and 75:25vol%, respectively. The X-ray diffraction patterns of these composites confirmed both perovskite and tungsten bronze phases. The scanning electron micrographs indicated homogeneity between ceramic and cement. These composites showed combined characteristics of perovskite and tungsten bronze ceramics with a high dielectric and piezoelectric properties. The dielectric constant (ε_{RT}) and piezoelectric charge coefficient (d_{33}) were found optimum at 75:25vol% composite which showed promising results that are potential for sensing and actuating in intelligent structures or structural health monitoring applications.

Compozite constituite dintr-un material piezoelectric binar de tip perovskit (titanat-zirconat de plumb şi lantan: PLZT) – bronz de wolfram (niobat de plumb, bariu şi bismut: PBBiN) şi un ciment portland obişnuit: OPC au fost obținute prin metoda reacțiilor în fază solidă. Materialul compozit a fost preparat pentru rapoartele ceramică/ciment de 25:75 %vol, 50:50%vol şi respectiv 75:25%vol. Difractogramele acestor materiale compozite confirmă existența ambelor faze (perovskitică şi bronz de wolfram). Microscopia electronică cu baleaj indică omogenitate între ciment şi ceramică. Aceste compozite au prezentat caracteristici combinate, corespunzătoare atât ceramicilor perovskitice precum şi a celor cu structură de tip bronz de wolfram, având proprietăți dielectrice şi piezoelectrice ridicate. Constanta dielectrică (ε_{RT}) şi coeficientul piezoelectric de sarcină (d_{33}) prezintă valori optime pentru compozitul cu raport 75:25%vol, ceea ce demonstrează obținerea unor rezultate promițătoare cu aplicații potențiale în domeniul senzorilor, actuatorilor, a structurilor inteligente sau pentru monitorizarea stării structurii în construcții.

Keywords: *A. Solid State Reaction; D. Composite Cement; b. Dielectric properties; b. Piezoelectric properties; Structural Health Monitoring*

1. Introduction

Piezoelectric ceramics have proven to be one of the most efficient materials for sensors and actuators in intelligent structures or structural health monitoring and vibration control of structures [1-3]. Recently, many piezoelectric materials have been fabricated and used in civil engineering structures. However, the traditional piezoelectric materials, such as piezoelectric polymer and polymer based piezoelectric composite, have poor compatibility with concrete [4]. It is also known in civil engineering that cement based materials are the most commonly used structural material. In contrast to structural materials used in the other fields, such as metals and alloys, which are produced in factories and are stable in structure, concrete is cast on site. It is well known that the hydration of concrete is a tedious and continuous process that perseveres for decades [5]. The hydration and dehydration process (i.e. expansion and contraction) of the concrete is greatly influenced by the change in water status. The traditional piezoelectric materials do not contract synchronistically with concrete, so they are not suitable for civil engineering applications. In order to overcome this setback and to meet the requirements, cement based piezoelectric composites that have good piezoelectric properties are most compatible with civil engineering structural applications [6]. The study of cement based piezoelectric ceramic composites has been extensively studied and made a great progress. However, a lot of setbacks exist and still remain to be solved. Cement based piezoelectric ceramic composites with excellent sensor properties and different connectivities need to be studied and developed further [7]. Non-destructive means can be used as in situ evaluation of these composites.

Lead zirconate titanate (PZT)– Ordinary

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Portland Cement (OPC) composite [8] was fabricated using 40%, 50% and 60% of PZT by volume for dielectric properties. The dielectric constants of the composites were found to be 139, 176 and 290 for composites containing 40%, 50% and 60% of PZT by volume, respectively. Porous lead zirconate titanate (PZT) ceramics [9] were fabricated by introducing pore-forming agent polymethyl methacrylate (PMMA) and sintering green compacts at low temperature. The phase, the microstructure, and the ferroelectric properties of the prepared ceramics were characterized. The correlation of microstructure with ferroelectric properties was discussed. Different methods and cement types were used in the above studies. The dielectric and piezoelectric properties of the PZT-cement composites were investigated [10]. It is well known that PZT composites are most commonly used since they have high piezoelectric planar and thickness electromechanical coefficients.

The PZT-ceramic composites have been extensively investigated. However, there still exists many material and structural issues. In this study, we report a smart composite with unique binary structured PLZT-Perovskite and PBBN-Tungsten Bronze with OPC composite for dielectric and piezoelectric properties.

The influence of two distinctly structured materials on the piezoelectric properties of the composites has been studied.

The main objective of this study was twofold: (i) To synthesize smart ceramic-cement composite with both sensing and actuating applications and (ii) the dependence of the dielectric and piezoelectric properties of cement based piezoelectric composites for structural health monitoring for non-destructive testing are reported. The composites synthesized have been represented in Table 1.

Table 1

Compositions synthesized 0.5PLZT-0.5PBBiN-Cement Composite

Formula compozitelor sintetizate 0.5PLZT-0.5PBBiN-Ciment

Composition	Formulae		
General Formula	$x(0.5[Pb_{1-x}La_x(Zr_zTi_{1-z})_{(1-(x/4))}]O_3\text{-}0.5[Pb_{(1-k-3z/2)}Ba_kBi_zNb_2O_6])\text{-}(1-x)OPC$		
Chemical formulae	$x(0.5[Pb_{0.988}La_{0.012}(Zr_{0.53}Ti_{0.47})_{0.997}O_3]\text{-}0.5[Pb_{0.557}Ba_{0.38}La_{0.022}Bi_{0.02}Nb_2O_6])\text{-}(1-x)OPC$		
PLZT-PBBiN-OPC – Perovskite Ceramic + TB-Ceramic + Original Portland Cement			
	PLZT-PBBiN-OPC-1	PLZT-PBBiN-OPC-2	PLZT-PBBiN-OPC-3
Ceramic vol%	25	50	75
Cement vol%	75	50	25

2. Experimental

Synthesis of 0.5PLZT-0.5PBBiN-Cement Composite:

Analytical reagent grade (99.99% purity) starting materials PbO, La_2O_3, ZrO_2, TiO_2, $BaCO_3$, Bi_2O_3, and Nb_2O_5 were subjected to solid state reaction method for the synthesis of perovskite-tungsten bronze structured ceramic powders. An excess 5wt% PbO was added to compensate lead loss. The stoichiometric powder was ball milled using zirconia balls and ethanol as media for 24 h. The dried powder was calcined at 900°C for 2 h in a high purity alumina crucible. Calcined powder was ball milled using zirconia balls and ethanol as media for 24 h to crush agglomerates and to minimize the particle size. The calcined and ground powder was sintered at 1050°C for 2 h.

The sintered powder and original Portland cement were ground well individually to obtain fine particles. These powders were then mixed thoroughly as ceramic to cement in the ratios of 25:75vol%, 50:50vol% and 75:25vol% of powders, respectively. A few drops of water was added in the individual mixtures and mixed well. The mixtures were pressed into circular discs of 12 mm diameter and 2 mm thickness at 80 MPa to form ceramic-cement composites. The compacted discs were cured at 60°C for 72 h with 98% relative humidity in order to obtain dense ceramic-cement composites.

Structural characterization of 0.5PLZT-0.5PBBiN-Cement Composite:

The phase formation in the ceramic-cement composites were analyzed by X-ray diffraction (XRD) technique (Philips X-ray diffractometer PW-1710) using CuK_α radiation with Ni filter at room temperature and a step scan from 2θ = 20 to 50°. As-cured composite surfaces were polished and gold coated using a sputtering technique to analyze microstructure. Microstructural studies were observed through scanning electron microscopy (SEM) of JEOL Model JSM-6380.

Electrical characterization of 0.5PLZT-0.5PBBiN-Cement Composite:

The polished composite surfaces were

painted with air dry silver paste to form perfect electrodes on the composite surfaces and these composites were characterized for room temperature dielectric constant (ε_{RT}) and dissipation factor (tanδ) at 1 kHz using 4192A HP Impedance analyzer. The electroded composites were poled in silicon oil bath at 100°C by applying a dc field of 40kV/cm. After 48 h ageing, the poled composites were characterized for piezoelectric charge coefficient (d_{33}) by using a Berlincourt piezo-d-meter.

3. Results and discussion

Figure 1 shows binary structured perovskite and tungsten bronze system. Piezoelectricity is one of the most widely used of the active materials. Its high stiffness gives the high actuating ability and can be easily controlled through an applied voltage. Furthermore, it also has high bandwidth, which allows a greater range of applications. Piezoelectricity has typically been utilized as actuator and sensor in vibration suppression system in structure. We have been systematically studying various perovskite and tungsten bronze composites of piezoelectric and pyroelectric materials, respectively. In the present investigation, we have obtained optimum results with the combination of cement with both perovskite and tungsten bronze structured composite. It is known that if a piezoelectric sensor material when embedded in concrete, the energy transfer between the piezoelectric sensor and the host concrete materials would be degraded by such mismatching. By introducing the cement as a passive medium, the properties of the piezoelectric cement composites can be customized for various applications namely acoustic impedance, vibration control or structural health monitoring with non-destructive testing is possible.

Figure 2 shows X-ray diffraction patterns of 0.5PLZT-0.5PBBiN-Cement Composite. The morphotrophic phase boundary (MPB) ceramic composition of 0.5PLZT and 0.5PBBiN was chosen in our study to achieve maximum piezoelectric properties. It is clear from figure 1 that the tetragonality peak splitting confirms tetragonal perovskite PLZT while the orthorhombic peaks confirm tungsten bronze structured PBBiN. As ceramic volume increases the phase formation and crystallinity is predominant in XRD patterns. The coexistence of perovskite and tungsten bronze phases (tetragonal and orthorhombic), respectively, existing in ceramic volume in forming cement composite structure for modifying the polycrystalline ceramic properties is evident from figure 2. The X-ray diffraction peaks showed a mixture of perovskite tetragonal phase and tungsten bronze orthorhombic phase with peculiar peaks due to the ceramic-cement composite. It is reported that the XRD peaks of PZT-OPC resembled the XRD peaks of PZT cement and where the increase in the intensities was observed with increasing PZT volume content [10]. A similar trend was observed in our study where the tetragonality and orthorhombicity increased as the ceramic volume increased in the ceramic-cement composite.

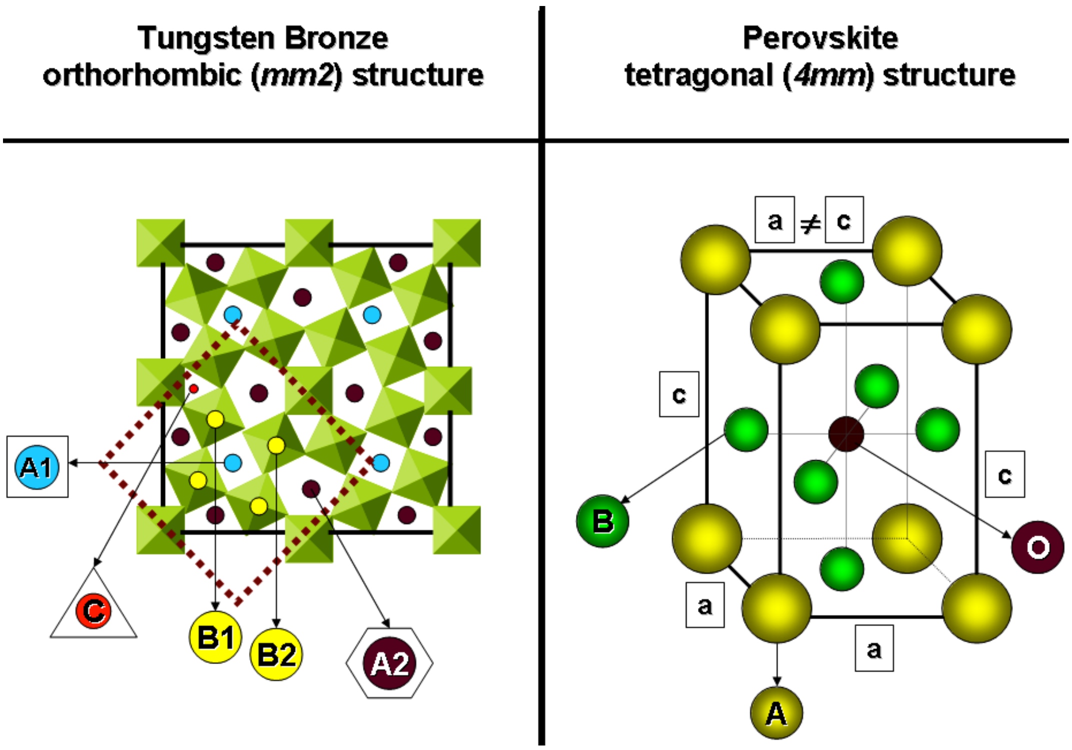


Fig. 1 - Tungsten Bronze and perovskite structures / *Structuri de tip bronz de wolfram şi perovskit* .

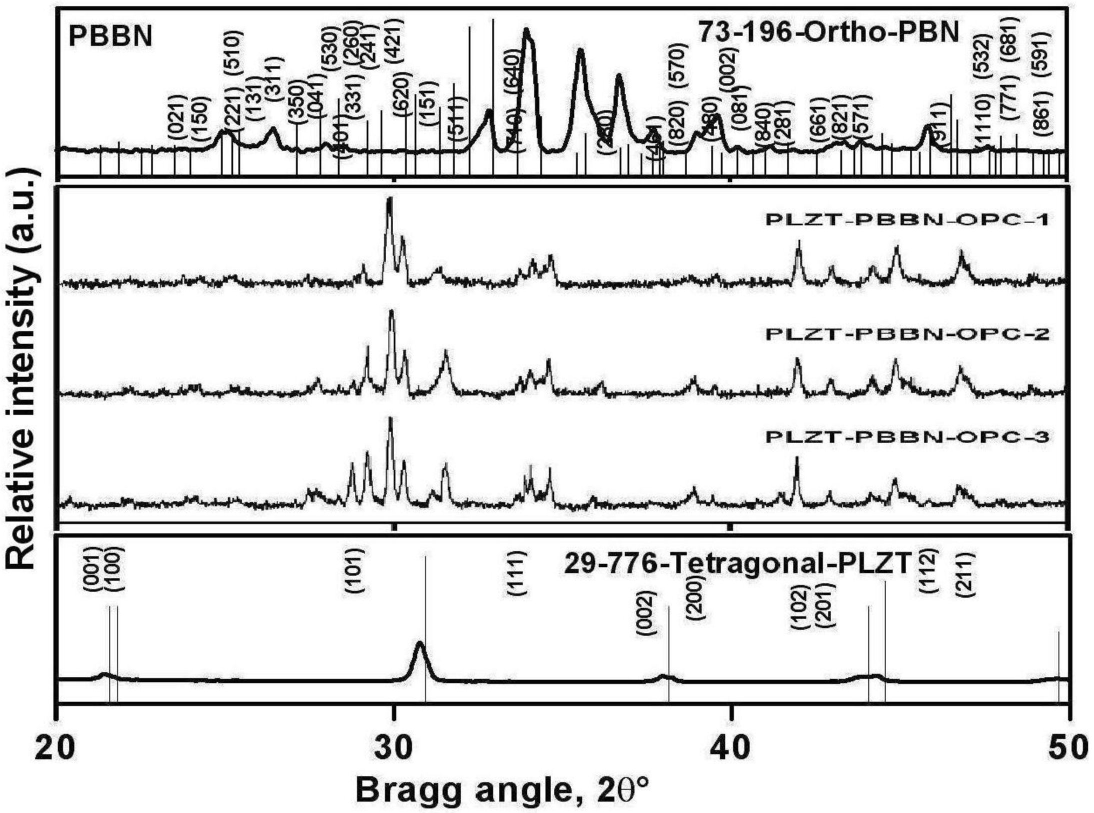
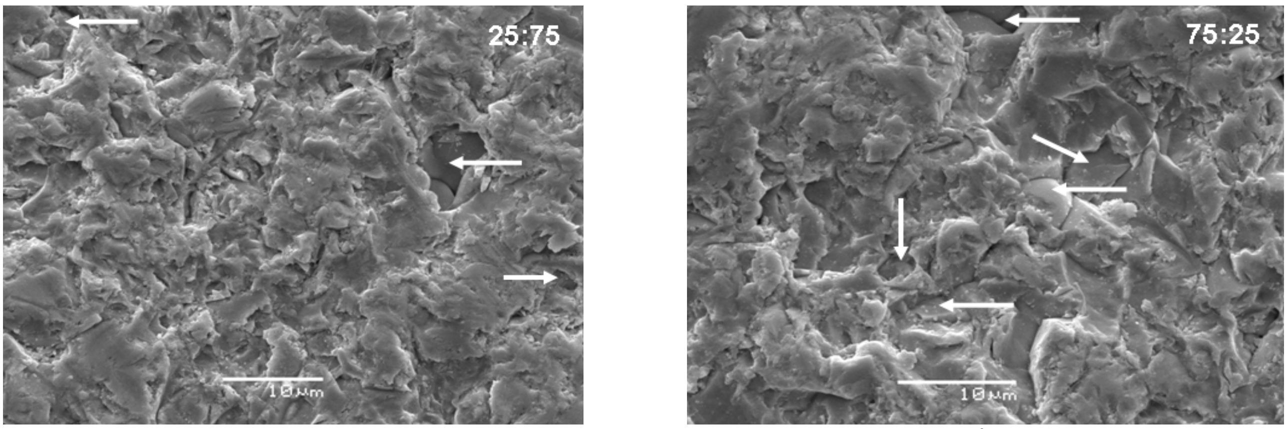


Fig. 2 - X-ray diffraction patterns of 0.5PLZT-0.5PBBiN-Cement Composite / *Difractogramele compozitelor 0.5PLZT-0.5PBBiN-Ciment.*



a b

Fig. 3 - Scanning electron micrographs of ceramic-cement 25:75 vol% (a) and 75:25vol% composites, respectively (b) / *Imagini SEM ale compozitelor de tip ceramică:ciment 25:75 % vol (a) şi respectiv 75:25% vol. (b)*

Figure 3 shows the scanning electron micrographs of ceramic-cement 25:75 vol% and 75:25vol% composite, respectively. The scanning electron micrograph reveals a typical microstructure of the ceramic-cement composite at the interfacial zone between ceramic volume and the cement volume where the grains can be clearly seen next to the cement hydration. It is clearly evident from the scanning electron micrographs that the grains are pore free and uniformly spread in the ceramic-cement composite which is homogenous in nature. The arrow mark in the SEM pictures indicates grains on ceramic-cement composite. It is well known that the homogeneous grains combined with high density result in high piezoelectric performance with excellent electromechanical properties of the composite. It is well known that the poling process occurs by the reversal of 180° domains and the rotation of 90° domains, with a relatively small fraction of domains actually remaining in an altered configuration upon removal of the applied field [11].

Figure 4 shows dielectric constant (ε_{RT}) and dielectric loss (tanδ) of 0.5PLZT-0.5PBBiN-Cement Composite. The dielectric constant increased as the ceramic vol% increased and reached the maximum at 75-25vol% composite having ε_{RT} = 534. It is reported that the porosity of the composite reduces with the increasing of ceramic/cement ratio and the influence of pore structure on the mechanical and dielectric properties of the composite are discussed [12]. On the other hand, in our study the cement based ceramic composite at the surface of 0.5PLZT-0.5PBBiN grains and Cement particles, the microstructure clearly shows that the grains are pore free and dense in nature. In fact, during cement hydration process, the chemical reaction of the 0.5PLZT-0.5PBBiN ceramic grains and cement particles becoming denser resulting in pore-free dense ceramic-cement composite. It is

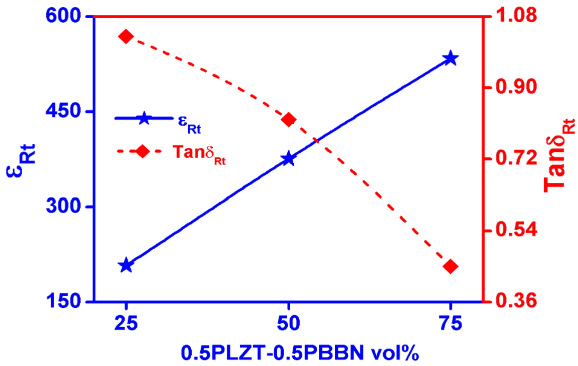


Fig. 4 - Dielectric constant (ε_{RT}) and dielectric loss (tanδ) of 0.5PLZT-0.5PBBiN-Cement composites / *Constanta dielectrică (e_{RT}) şi pierderile dielectrice (tanδ) corespunzătoare compozitelor 0.5PLZT-0.5PBBiN-ciment.*

observed that the dielectric values increased as the ceramic volume increased in the composite. The dissipation factor (tanδ) decreased continuously as ceramic volume increased. The higher the ceramic content the greater the dielectric properties were achieved. As reported in literature, the highest dielectric constant achieved was 291 [10] whereas in our study, we observed a value of ε_{RT} = 534 in the investigated domain, which is superior to the values reported.

Figure 5 shows piezoelectric coefficient (d_{33}) of 0.5PLZT-0.5PBBiN-Cement Composite. It is observed that the piezoelectric coefficient (d_{33}) is strongly influenced by the ceramic volume in the composite. The piezoelectric coefficient (d_{33}) increased up to 75:25vol% ceramic-cement composite. It is well known that the pore free, uniform and homogenous grains contribute to the piezoelectric effect from the perovskite and tungsten bronze in the composite. It is reported that the piezoelectric d_{33} increases as the P(LN)ZT volume fraction increases explaining the polarization behavior [13]. The well-densified and pore-free grains contributed to the piezoelectric effect in our study. The maximum piezoelectric coefficient (d_{33}) was observed in 75:25vol% ceramic-cement composite. The dielectric constant followed a similar trend with the d_{33}. It is observed that piezoelectric materials such as PZT-cement composites have good compatibility with civil engineering structural applications [14]. The results show that d_{33} values of PLZT-PBBN-OPC composites increased with increasing ceramic volume (d_{33} of 25:75vol%=29 pC/N, d_{33} of 50:50vol%=52 pC/N and d_{33} of 75:25vol% = 87 pC/N). The ceramics poled under similar conditions using similar size of composite discs showed different behavior due to the increase of ceramic volume in the composite. We have observed the highest d_{33}=87 pC/N value for 75:25vol% ceramic-cement composite in the investigated domain which is amongst the highest reported when compared to the literature [10].

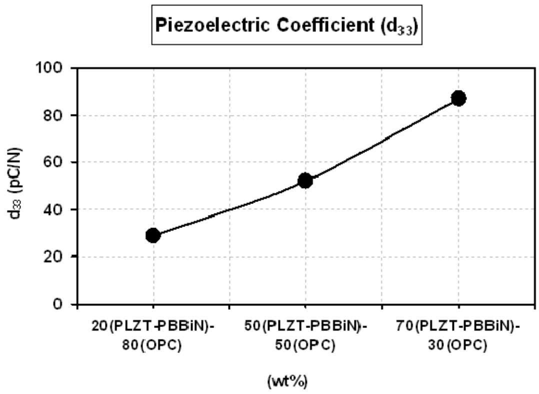


Fig. 5 - Piezoelectric coefficient (d_{33}) of 0.5PLZT-0.5PBBiN-Cement Composites / *Coeficientul piezoelectric (d_{33}) al compozitelor 0.5PLZT-0.5PBBiN – ciment.*

4. Conclusion

The PLZT-PBBN-OPC ceramic-cement composites have shown binary structured perovskite tetragonal and tungsten bronze orthorhombic phases in the lattice exhibiting incredible dielectric and piezoelectric properties. Scanning electron micrograph pictures indicated that pore-free grains which was uniformly spread in the ceramic-cement composite and homogenous in nature. The dielectric constant increased as the ceramic volume was increased in the composite whereas the dissipation factor decreased. The dielectric constant was found to be optimum at 75:25vol% ceramic-cement composite. The maximum piezoelectric coefficient d_{33} was obtained in 75:25vol% ceramic-cement composite. The novelty behavior of these composites is the exhibition of excellent dielectric and electromechanical properties which supports both sensing and actuating process in a single system and 75:25vol% ceramic-cement composite could be used for non-destructive testing in situ structural health monitoring applications.

ACKNOWLEDGEMENTS

The financial support from FONDECYT with research grant under Project N°1080635 is greatly acknowledged. The authors would like to acknowledge University of Concepcion, Chile and Andhra University, India. We would also like to thank Ms. C. N. Devi, Mr. Ranganathan and Mr. Krishnamurthy for their technical support extended during this work.

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