

# Metal Dielectric High Permittivity composites for High K Applications

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## ABSTRACT

The Bismuth Zinc Niobate-Silver (BZN-Ag) composites were prepared by solid-state ceramic route. Sintering temperature of BZN-Ag composites were lowered to 850°C/2hrs. The structure and surface morphology of the composites were investigated using XRD and optical microscope. The dielectric and conducting properties of the composites were systematically investigated with the volume fraction of silver in the frequency range from 1 KHz to 1 MHz. The dielectric constant of the composite increases with silver content and it is in good agreement with power law below the percolation limit. Addition of 0.14 volume fraction of silver increases the dielectric constant of BZN+2wt% B<sub>2</sub>O<sub>3</sub> from 150 to 2350 at 1 MHz. However, 15 volume percentage of silver loading results a giant permittivity of ( $\epsilon_r$ )  $\approx 10^5$  with low dielectric loss ( $\tan\delta \approx 10^{-2}$ ) at 1 MHz. Subsequent increase in silver loading decreases the dielectric constant. The BZN-B<sub>2</sub>O<sub>3</sub>-Ag composite with giant permittivity may find applications in electromechanical and tunable devices.

**Keywords:** *percolation, composites, cermets, BZN, Silver.*

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## I. INTRODUCTION

Recently, considerable attention has been paid to high dielectric constant composites, because of their potential for a wide range of technologically important applications such as high k gate dielectrics,<sup>1</sup> capacitor dielectrics<sup>2</sup> and electrostrictive materials.<sup>3,4</sup> High dielectric constant, reasonably low loss and low processing temperature are the basic requirements of these materials for such applications. In the context of high dielectric constant materials, several polymer-metal composites<sup>5-8</sup> and ceramic-metal composites<sup>9-17</sup> have been studied. As the volume fraction of metals or conducting phases in these composites increase, the dielectric constant and conductivity increases gradually and when the volume fraction of the conductive powder reaches a critical value, the conductivity as well as dielectric constant of the composite increases by several orders of magnitude.<sup>18</sup> This critical value is referred to as percolation limit of the composite. Several groups have reported such increase in dielectric constant and conductivity in the neighborhood of percolation threshold.<sup>9,19,20</sup> The conducting powders used in ceramic metal composites are Pt, Pd, Ag, Al, Cu, Ni, etc. Out of these Pt, Pd etc are too expensive and Al, Cu, Ni have oxidizing problem while sintering at higher temperatures. So these cannot be considered as

possible candidate for practical applications. Nickel containing composites<sup>9-12</sup> give high dielectric constant, consistent with percolation law. But these are sintered at high temperatures in an inert atmosphere. Silver containing composites do not have such drawbacks and show excellent permittivity near the percolation threshold.<sup>13-17</sup> It is noted that all the ceramic-silver composites reported so far were sintered at the sintering temperature of ceramics, which is much above the melting point of silver. Several previous reports show that silver can diffuse along open pores in the ceramics at higher temperatures and escape from the surface, since the melting point of silver (961°C) is lower than the sintering temperature used for the ceramic-Ag composites.<sup>21-24</sup> This loss of silver during sintering of ceramic-Ag composites and its impact on the properties were ignored in the earlier studies.<sup>15,16</sup> Even the amount of silver present in such composites after the sintering can vary depending on the sintering temperature. Therefore, it is necessary to lower the sintering temperature of composite to prevent the loss of silver. There had been several attempts to lower the sintering temperature of ceramic systems by the addition of low melting glasses,<sup>25,26</sup> especially in the context of lowering the sintering temperature of dielectrics below 961°C for low temperature co-fired ceramic (LTCC) applications.

The  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  (BZN) composition is a widely studied tunable dielectric material, which has dielectric constant of about 150, dielectric loss of  $10^{-4}$ , tunability of above 50% at 2.4 MV/cm and the sintering temperature is about 1050°C/2hrs.<sup>27-29</sup> In this paper, we report the preparation of high permittivity BZN-Ag composites by lowering the sintering temperature of BZN below the melting point of silver by the addition of  $\text{B}_2\text{O}_3$  glass. The effect of different volume fractions of silver in BZN matrix on the dielectric and conducting properties in the frequency range from 1 KHz to 1 MHz are investigated.

## **II. EXPERIMENTAL**

The  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  ceramic samples were prepared by the conventional solid state ceramic route. High purity  $\text{Bi}_2\text{O}_3$ , ZnO (99.9+%, Aldrich chemical company, Inc, Milwaukee, WI, USA) and  $\text{Nb}_2\text{O}_5$  (99.9+%, NFC Hyderabad, India) were used as the starting materials. Stoichiometric amounts of the powder samples were mixed and ball milled using zirconium balls in distilled water medium for 24 hours. The resultant slurry was then dried and calcined at 900°C for six hours. Different weight percentages of  $\text{B}_2\text{O}_3$  are added to the fine powder of calcined material in order to reduce the sintering temperature below 961°C. Two-weight percentage of  $\text{B}_2\text{O}_3$  was found to be optimum to achieve this reduction in sintering temperature. Subsequently calcined BZN powder with 2 weight percent of  $\text{B}_2\text{O}_3$  powder was prepared by mixing in distilled water medium followed by drying and grinding. Different volume fractions of silver (99.99%, -60 mesh, Aldrich chemical company, Inc, Milwaukee, WI, USA) were added to this powder and mixed again in distilled water medium. Polyvinyl alcohol (PVA) (Molecular Weight 22000, BDH Lab Suppliers, England) solution was then added to the powder, mixed, dried and ground well. The powder containing BZN,  $\text{B}_2\text{O}_3$  and silver was pressed into cylindrical disks of about 11 mm diameter and 1mm thickness, by applying a pressure of 100 MPa. These compacts were sintered at different temperatures from 825°C to 975°C for 2 hours. Electrodes were connected to both sides of the sintered and polished compacts using silver paste and these samples were used for measuring the dielectric properties. The dielectric properties were measured using a LCR meter (HIOKI 3532-50 LCR Hi TESTER, Japan). The crystal structure and phase purity of the powdered samples were studied by X- ray diffraction technique using

Ni-filtered Cu-K $\alpha$  radiation using Rigaku Dmax-I, Japan diffractometer. The surface morphology and microstructures of the sintered samples were studied using an optical microscope (Leica, DMRX, Germany) and scanning electron microscope (JEOL-JSM 5600 LV, Tokyo, Japan).

### III. RESULTS AND DISCUSSION

X-ray diffraction patterns of sintered BZN-Ag composites with different volume fractions of silver are shown in Fig.1. Figure 1a is the XRD pattern of BZN with 2wt% B<sub>2</sub>O<sub>3</sub> sintered at 950°C/2hrs, while Fig.1b, c and d corresponds to the XRD patterns of composites with 10, 15 and 18 volume percentages of silver sintered at 850°C/2hrs. In the X-ray diffraction patterns all peaks were identified as those due to BZN (indexed as cubic pyrochlore JCPDS 54-971) and metallic silver (JCPDS 03-0921). This indicates that no phases other than BZN and silver were present in the matrix sintered at 850°C/2hrs.

The variation of dielectric constant, dielectric loss and conductivity of the BZN-Ag composites were studied as a function of silver content, sintering temperature and frequency. Fig. 2 shows the variation of percentage density of BZN, BZN+B<sub>2</sub>O<sub>3</sub> and BZN+B<sub>2</sub>O<sub>3</sub>+Ag at different sintering temperatures. The sintering temperature of the composite was optimized for the maximum density. It is found that pure BZN sintered at 1050°C/2hrs and addition of 2wt% B<sub>2</sub>O<sub>3</sub> glass lowered the sintering temperature to 950°C/2hrs. As the sintering temperature of BZN+2wt% B<sub>2</sub>O<sub>3</sub>+Ag composite increased, the density increased and showed maximum density at 850°C/2hrs and there after decreases. This could be due to the fact that as the sintering temperature increased, the silver in the matrix melts and comes out to the surface and escapes during heating as well as polishing. Fig. 3 shows the optical micrograph of the unpolished BZN+2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites (with 0.15 volume fraction of silver) sintered at different temperatures. Fig.3a and b clearly shows that the silver particles agglomerate as the sintering temperature increases from 850°C to 900°C/2hrs. As the temperature is further increased to 950°C and 975°C/2hrs, silver melts and comes out of the matrix as bubbles as shown in Fig.3c and d. It also strongly supports the report of evaporation of silver at higher temperatures.<sup>21-24</sup>

The effect of sintering temperature on the dielectric constant of BZN+2wt% B<sub>2</sub>O<sub>3</sub> ceramics for different volume fraction (V<sub>f</sub>) of silver at frequencies of 1 KHz, 10 KHz, 100 KHz and 1 MHz are shown in Fig. 4. As the sintering temperature is increased, the dielectric constant of the composites increased to a maximum value at 850°C/2hrs and then decreased. The dielectric constant decreased when the samples were sintered above 850°C at all frequencies. The variation in permittivity is more at lower frequencies and as the frequency increased the variation is decreased. The variation in dielectric constant with sintering temperatures were more prominent for those composites with silver content more than the percolation limit at all frequencies. For composites containing less silver than the percolation limit, the variation was much more gradual. Thus it becomes obvious that addition of silver reduces the sintering temperature of the BZN+B<sub>2</sub>O<sub>3</sub> ceramic. It is reported that the silver addition lowered the sintering temperature of the ceramics.<sup>15</sup> In BZN+2wt% B<sub>2</sub>O<sub>3</sub>+Ag, the presence of B<sub>2</sub>O<sub>3</sub> lowers the sintering temperature of silver to below the melting point (961°C). At sintering temperatures below 950°C, the Ag particles are distributed in BZN matrix. As the sintering temperature increases, the Ag particles moved along the grain boundary and get concentrated at the grain boundary intersections.<sup>30</sup> This means that, the

agglomeration of Ag particles occurred at higher temperature. Hence the size of silver particles increase with sintering temperature and results in increased inter particle distance (distance between two Ag particle) and decreased number of Ag particles. In addition silver can also escape from the matrix at higher temperature as can be seen from Fig. 3c and d. This can lead to a decrease in dielectric constant with increase in temperature. Thus the optimum sintering temperature of the composite was found to be 850°C/2hrs.

The variation of dielectric constant, dielectric loss and conductivity with different volume fraction of silver at 1 KHz, 10 KHz, 100 KHz and 1 MHz sintered at 850°/2hrs is as shown Fig. 5. An abrupt increase of dielectric constant ( $\epsilon_r \approx 10^5$ ) is observed at 0.15 volume fraction of silver and this is taken as the percolation threshold. The sharp increase of dielectric constant can be explained by two mechanisms; the generation of dielectric field around conducting particle and the formation of micro-capacitors through the isolation of silver with thin dielectric layers. It is reported that dielectric field is developed around the conducting particles dispersed in insulating materials.<sup>31,32</sup> The sharp increase in dielectric constant is a result of an interfacial polarization phenomenon which occurs at the interface of the dissimilar materials.<sup>33</sup> The charge carriers in the different phases of the composite are trapped at the interfaces within the dielectrics. These charges are unable to discharge freely and give rise to an over all field distortion, which results in an increase in capacitance and dielectric constant. In BZN+2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites, the dielectric field developed around the silver particle can result in an increase of effective dielectric constant. There are regions in the microstructure where the conductive clusters are separated by a thin insulating layer. The silver particles in the composites act as internal electrodes of unit micro-capacitor. Such regions contribute to extremely large capacitance, which adds up macroscopically and result in a giant effective dielectric constant. It can be seen from Fig. 5 b that the dielectric loss also increases sharply at percolation threshold. The addition of silver increases the defects and induces space charge. Therefore the increase in dielectric loss could be due to increase in metallic silver in the composite. It is well known that ceramic metal composite can have insulator-metal transition with increasing metal concentration. An abrupt change in conductivity at percolation in BZN+2wt% B<sub>2</sub>O<sub>3</sub>+Ag composite with different volume fractions of silver is as shown in Fig. 5 c. As the volume fraction is increased, the clusters of silver begin to merge and at the percolation limit, there is a continuous path of adjacent allowed sites across the system. This leads to the sudden increase in conductivity. The insulator-metal transitions are characterized by an abrupt change in conductivity.<sup>5</sup>

Figure 6 shows the dielectric constant of BZN+2wt% B<sub>2</sub>O<sub>3</sub>+Ag composite with different volume fraction of silver at 1 MHz sintered at 850°C/2hrs. It is observed that as the silver content increases from 0 to 0.14-volume fraction, the dielectric constant increases from 150 to 2340 with dielectric loss of 10<sup>-3</sup>. The concentration dependence of dielectric constant is given by the following power law on the basis of percolation theory.<sup>34</sup>

$$\epsilon(v) = \epsilon_o \left( \frac{V_c - V}{V_c} \right)^{-q} \quad (1)$$

where  $\epsilon_0$  is the dielectric constant of pure silver free BZN,  $V_c$  is the volume fraction of silver at percolation,  $V$  is the volume fraction of silver and  $q$  is a critical exponent. The experimental values of effective dielectric constant are in good agreement with that calculated using equation-1, with  $q=0.86$  and  $V_c=0.15$  as shown in Fig. 6.

Fig. 7 shows the optical micrograph of BZN+2wt%  $B_2O_3+Ag$  composite with different volume fraction of silver sintered at  $850^\circ C/2hrs$ . It can be observed in the micrograph that silver particles (white area) are distributed in the BZN matrix and some silver particles are lost during polishing (black area). The spacing between Ag particle decreased with increasing Ag concentration and no apparent interconnection among particles is observed for samples with silver less than the percolation limit. But above the percolation threshold, the silver particles agglomerated to become larger size is as shown in Fig. 7 c. The optical micrograph clearly reflects the dispersion of Ag particle in the BZN matrix. Fig. 8 shows the scanning electron micrographs of BZN+2wt%  $B_2O_3+Ag$  composite with different volume fraction of silver sintered at  $850^\circ C/2 hrs$ . It is found that grain size decreases with increase in silver content and it is in good agreement with pervious reports.<sup>12,15</sup> This could be due to that fact that silver addition hindered the grain growth of ceramic matrix and decreased the grain size with increase in silver content. It is reported that silver particles were primarily located at grain boundaries when sintering was performed below  $900^\circ C$ .<sup>35</sup> It can be seen from Fig. 8 that as the volume fraction of silver in the composite increases, more silver is found at the interface. The reduction of grain size with silver content increases number of defect and induces change in distribution of space charge. This space charge generates dipole moment in an external electric field. The reduction of grain size increases the defects and in turn modifies the accumulation of space charge in the grain boundaries. Thus the reduction of grain size has obvious dependence on the defect and thereby distributions of space charge.

The variation of conductivity of BZN+2wt%  $B_2O_3+Ag$  composites with frequency for different volume fractions of silver sintered at  $850^\circ C/2hrs$  are shown in Fig. 9. It can be noticed that as the silver content in the composite increases the conductivity increases. Composites containing silver less than the percolation limit show gradual increase in conductivity while those with more silver than the percolation limit show conductivity values that are several orders higher. As the frequency increases the conductivity increases to a maximum value for composites containing less silver than that of the percolation limit. However subsequent increase in silver content in the composite beyond the percolation limit decreases the conductivity with increase in frequency.

Fig. 10 shows the variation of dielectric constant of BZN+2wt%  $B_2O_3+Ag$  composites with frequency for different volume fraction of silver sintered at  $850^\circ C/2hrs$ . As described earlier the dielectric constant increases gradually with silver content when the volume fraction is less than the percolation limit. When the silver content is beyond the percolation limit, the dielectric constant also increases by several orders of magnitude. It is found that dielectric constant decreases with increase in frequency above percolation threshold. Because of its direct relation to polarization, relative permittivity can have strong frequency variation as different polarization mechanisms become active. Inset of Fig. 10 shows the variation of dielectric constant of BZN+2wt%  $B_2O_3+0.14Ag$  composites with frequency.

High permittivity ceramics are ferroelectrics having  $\epsilon_r$  of the order of  $10^3$  with relatively high dielectric loss compared to low loss dielectric ceramics ( $\epsilon_r < 300$ ). It is well known that enhanced electrostriction is related to the enhanced dielectric constant. This suggests that the electrostriction can be enhanced by increasing the



dielectric constant of the composite, so that same electric field can induce higher polarization and thus higher electrostriction. In the present ceramic metal composite (BZN-B<sub>2</sub>O<sub>3</sub>-Ag), the relative permittivity is very high of the order of 10<sup>5</sup> with low dielectric loss ( $\tan\delta\approx 10^{-2}$ ) at 1 MHz as compared to BaTiO<sub>3</sub> and PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> ceramics and its silver composites.<sup>14,15</sup> The BZN-B<sub>2</sub>O<sub>3</sub>-Ag composite were sintered at 850° C, which is lower than the melting point of silver and hence the evaporation of silver during sintering is avoided compared to BaTiO<sub>3</sub>-Ag and PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>-Ag composites.

#### **IV. CONCLUSIONS**

BZN ceramics are prepared by solid state ceramic route at temperatures less than the melting temperature of silver (961°C) by the addition of 2 wt% of B<sub>2</sub>O<sub>3</sub> glass. Silver addition to the BZN-B<sub>2</sub>O<sub>3</sub> ceramics further reduces the sintering temperature of the composite to 850°C/2hrs and hindered the grain growth of BZN. The BZN-B<sub>2</sub>O<sub>3</sub>-Ag composites sintered at 850°C/2hrs shows maximum density and dielectric constant. Dielectric properties of these composites increase with silver content according to the power law. A giant permittivity of 10<sup>5</sup> with low dielectric loss ( $\tan\delta\approx 10^{-2}$ ) at 1 MHz was observed for 0.15-volume fraction of silver. This offers the perspectives for application of this composite in LTCC and electromechanical devices.

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#### **REFERENCES**

- [1.] <sup>1</sup>F. Chen, C. Chu, J.He, Y. Yang, and J. Lin, "Organic thin-film transistors with nanocomposite dielectric gate insulator," *Appl. Phys. Lett.*, **85** [15] 3295-97 (2004).
- [2.] <sup>2</sup>Y. Rao, S. Ogitali, P. Kohl, and C. P. Wong, "Novel polymer-ceramic nanocomposite based on high dielectric constant epoxy formula for embedded capacitor application," *J. Appl. Polym. Sci.*, **83** [5] 1084-90 (2002).
- [3.] <sup>3</sup>C. Huang, Q. M. Zhang, and J. Su, "High-dielectric-constant all-polymer percolative composites," *Appl. Phys. Lett.*, **82** [20] 3502-04 (2003).
- [4.] <sup>4</sup>C. Huang, Q. M. Zhang, G. deBotton, and K. Bhattacharya, "All-organic dielectric-percolative three-component composite materials with high electromechanical response," *Appl. Phys. Lett.*, **84** [22] 4391-93 (2004).
- [5.] <sup>5</sup>Z.-M. Dang, Y.-H. Lin, and C.-W. Nan, "Novel Ferroelectric Polymer Composites with High Dielectric Constants," *Adv. Mater.*, **15** [19] 1625-29 (2003).
- [6.] <sup>6</sup>C. Huang and Q. Zhang, "Enhanced Dielectric and Electromechanical Response in High Dielectric Constant All-Polymer Percolative Composites," *Adv. Funct. Mater.*, **14** [5] 501-06 (2004).

- [7.] <sup>7</sup>Y.-J. Li, M. Xu, and J.-Q. Feng, Z.-M. Dang “Dielectric behavior of a metal-polymer composite with low percolation threshold,” *Appl. Phys. Lett.*, **89**, 072902-1-3 (2006).
- [8.] <sup>8</sup>J. Y. Li, C. Huang, and Q. Zhang, “Enhanced electromechanical properties in all-polymer percolative composites,” *Appl. Phys. Lett.*, **84** [16] 3124-26 (2004).
- [9.] <sup>9</sup>C. Pecharroman, and J. S. Moya, “Experimental Evidence of a giant Capacitance in Insulator-Conductor Composites at the Percolation Threshold,” *Adv. Mater.*, **12** [4], 294-97 (2000).
- [10.] <sup>10</sup>C. Pecharroman, F. E. Betegon, J. F. Bartolome, S. L. Esteban, and J. S. moya, “New Percolative BaTiO<sub>3</sub>-Ni Composites with a High and Frequency-Independent Dielectric Constant ( $\epsilon_r \approx 80000$ ),” *Adv. Mater.*, **13** [20] 1541-44 (2001).
- [11.] <sup>11</sup>H.-W. Choi, Y.-W. Heo, J.-H. Lee, J.-J. Kim, H.-Y. Lee, E.-T. Park, and Y.-K. Chung: Effects of BaTiO<sub>3</sub> on dielectric behavior of BaTiO<sub>3</sub>-Ni-polymethyl methacrylate composites,” *Appl. Phys. Lett.*, **89**, 132910 (2006).
- [12.] <sup>12</sup>P.-H. Xiang, X.-L. Dong, C.-D. Feng, R.-H. Liang, Y.-L. Wang, “Dielectric behavior of lead zirconate titanate/silver composites,” *Mater. Chem. Phys.*, **97**, 410-14 (2006).
- [13.] <sup>13</sup>J. Xu, and C. P. Wong, “Low-loss percolative dielectric composite,” *Appl. Phys. Lett.*, **87**, 082907 (2005).
- [14.] <sup>14</sup>R. Z. Chen, X. Wang, Z. L. Gui, and L. T. Li, “Effect of Silver Addition on the Dielectric Properties of Barium Titanate-Based X7R Ceramics,” *J. Am. Ceram. Soci.*, **86** [6] 1022-24 (2003).
- [15.] <sup>15</sup>S. Panteny, C. R. Bowen, R. Stevens, “Characterisation of barium titanate-silver composites, part I: Microstructure and mechanical properties,” *J. Mater. Sci.*, **41**, 3837-43 (2006).
- [16.] <sup>16</sup>S. Panteny, C. R. Bowen, R. Stevens, “Characterisation of barium titanate-silver composites part II: Electrical properties,” *J. Mater. Sci.*, **41**, 3845-51 (2006).
- [17.] <sup>17</sup>N. Duan, J. E. ten Elshof, H. Verweij, G. Greuel, and O. Dannapple, “Enhancement of dielectric and ferroelectric properties by addition of Pt particles to a lead zirconate titanate matrix,” *Appl. Phys. Lett.*, **77** [20] 3263-65 (2000).
- [18.] <sup>18</sup>S. Kirkpatrick, “Percolation and Conduction,” *Rev. Mod. Phys.*, **45**, 574-88 (1973).
- [19.] <sup>19</sup>D. M. Grannan, J. C. Garland, D.B. Tanner, “Critical Behavior of the Dielectric Constant of a Random Composite near the Percolation Threshold,” *Phys. Rev. Lett.*, **46** [5] 375-78 (1981).
- [20.] <sup>20</sup>Y. Song, T. W. Noh, S. Lee, and J.R. Gaines, “Experimental study of the three-dimensional ac conductivity and dielectric constant of a conductor-insulator composite near the percolation threshold,” *Phys. Rev. B.*, **33** [2] 904-08 (1986).
- [21.] <sup>21</sup>S. Y. Cho, H. J. Youn, D. W. Kim, T.G. Kim, and D. S. Hong, “Interaction of BiNbO<sub>4</sub>-Based Low-Firing Ceramics with Silver Electrodes,” *J. Am. Ceram. Soc.*, **81** [11] 3038 –40 (1998).
- [22.] <sup>22</sup>C. Y. Chen and W. H. Tuan, “Evaporation of Silver during Cofiring with Barium Titanate,” *J. Am. Ceram. Soc.*, **83** [7], 1693-98 (2000).
- [23.] <sup>23</sup>A. L. Caballero, E. Nieto and P. Duran, “Ceramic–electrode interaction in PZT and PNN–PZT multilayer piezoelectric ceramics with AG/PD 70/30 inner electrode,” *J. Mater. Sci.*, **32**, 3257-62 (1997).
- [24.] <sup>24</sup>H. C. Ling, “Diffusion of Sputtered Vanadium, Nickel, and Silver in Lead Magnesium Niobate Ceramic,” *J. Am. Ceram. Soci.*, **72** [5] 770-74 (1989).

- [25.] <sup>25</sup>K. P. Surendran, P. Mohanan and M. T. Sebastian, "The effect of glass additives on the microwave dielectric properties of Ba(Mg<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramics," *J. Solid-State Chem.*, **177** [11] 4031-46 (2004).
- [26.] <sup>26</sup>P.V. Bijumon and M.T. Sebastian, "Influence of glass additives on the microwave dielectric properties of Ca<sub>5</sub>Nb<sub>2</sub>TiO<sub>12</sub> ceramics," *Materials Science and Engineering: B.*, **123** [1] 31-40 (2005).
- [27.] <sup>27</sup>H. Du and X. Yao, "Investigations on structural evolution and dielectric characteristics of high performance Bi-based dielectrics," *Mater.Res. Bull.*, **40** [9] 1527-35 (2005).
- [28.] <sup>28</sup>A. K. Tangantsev, J. Lu, and S. Stemmer "Temperature dependence of the dielectric tunability of pyrochlore bismuth zinc niobate thin films," *Appl. Phys. Lett.*, **86**, 032901 (2005).
- [29.] <sup>29</sup>X. Q. Wang, H. Wang, and X. Yao "Structures, Phase Transformations, and Dielectric Properties of Pyrochlores Containing Bismuth," *J. Am. Ceram. Soc.*, **80** [10] 2745-48 (1997).
- [30.] <sup>30</sup>H. J. Hawang, M. Yasunoka, M. Sando, M. Toriyama, and K. Niihara, "Fabrication, Sinterability, and Mechanical Properties of Lead Zirconate Titanate/Silver Composites," *J. Am. Ceram. Soc.*, **82** [9] 2417-22 (1999).
- [31.] <sup>31</sup>P. Chylek and V. Srivastava, "Effective dielectric constant of a metal-dielectric composite," *Phys. Rev. B.*, **30** [2] 1008-09 (1984).
- [32.] <sup>32</sup>W. J. Kaiser, E. M. Logothetis and L. E. Wenger, "Dielectric response of small metal particle composites," *J. Phys. C: Solid State Phys.*, **18**, L 837-42 (1985).
- [33.] <sup>33</sup>S. H. Foulger, "Reduced percolation thresholds of immiscible conductive blends," *J. Poly. Sci; Part B: Poly. Phys.*, **37** [15] 1899-1910 (1999).
- [34.] <sup>34</sup>E. L. Efors and B. I. Shktovskii, "Critical Behaviour of Conductivity and Dielectric Constant near the Metal-Non-Metal Transition Threshold," *Phys.Status. Solidi B.*, **76** [2] 475-85 (1976).
- [35.] <sup>35</sup>H. J. Hawang, M. Yasunoka, M. Sando, M. Toriyama, and K. Niihara, "Curie Temperature Anomaly in Lead Zirconate Titanate/Silver composites," *J. Am. Ceram. Soc.*, **81** [3] 709-12 (1998).

## FIGURE CAPTIONS

**Fig. 1.** XRD patterns of (a) BZN+2wt% B<sub>2</sub>O<sub>3</sub>, (b) BZN+2wt% B<sub>2</sub>O<sub>3</sub> + 0.1Vf of Ag, (c) BZN+2wt% B<sub>2</sub>O<sub>3</sub> +0.15Vf of Ag and (d) BZN+2wt% B<sub>2</sub>O<sub>3</sub> +0.18Vf of Ag in BZN-Ag composites sintered at 850°C/2hrs.

**Fig. 2.** Variation of percentage density with sintering temperature of BZN, BZN+B<sub>2</sub>O<sub>3</sub> and BZN+B<sub>2</sub>O<sub>3</sub> +0.15Ag.

**Fig. 3.** The optical micrograph of unpolished BZN +2wt% B<sub>2</sub>O<sub>3</sub>+ 0.15 Vf of Ag sintered at (a) 850 °C , (b) 900 °C, (c) 950 °C and (d) 975 °C/2hrs .

**Fig. 4.** Variation of dielectric constant of BZN+2wt% B<sub>2</sub>O<sub>3</sub>+Ag with sintering temperature for different volume fraction of silver at (a) 1 KHz, (b) 10 KHz, (c) 100 KHZ and (d) 1 MHz.

**Fig. 5.** The variation of (a) dielectric constant, (b) dielectric loss and (c) conductivity with different volume fraction of Ag at different frequency in BZN +2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites sintered at 850°C/2hrs.

**Fig. 6.** Variation of dielectric constant of BZN +2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites with different volume fraction of silver below percolation threshold sintered at 850°C/2hrs and the comparison with power law.

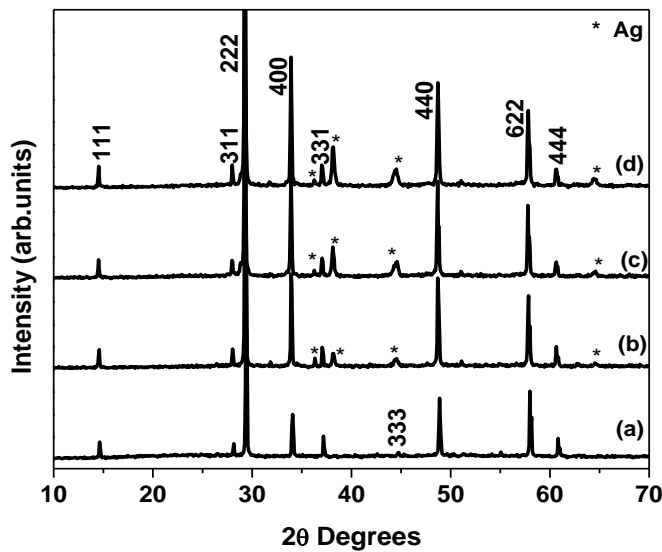
**Fig. 7.** The optical micrograph of BZN +2wt% B<sub>2</sub>O<sub>3</sub>+ (a) 0.10 Vf of Ag, (b) 0.15 Vf of Ag, and (c) 0.18 Vf of Ag composites sintered at 850°C /2hrs.



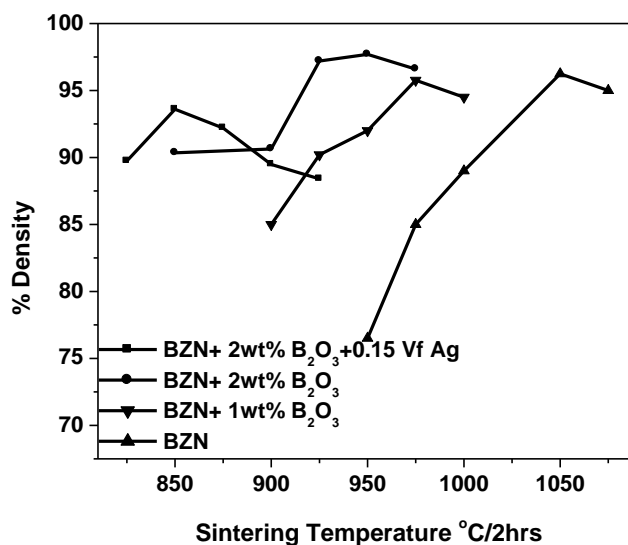
**Fig. 8.** The scanning electron micrographs of (a) BZN +2wt% B<sub>2</sub>O<sub>3</sub>, (b) BZN +2wt% B<sub>2</sub>O<sub>3</sub>+0.10 Vf of Ag and (c) BZN +2wt% B<sub>2</sub>O<sub>3</sub>+0.15 Vf of Ag composites sintered at 850°C/2hrs.

**Fig. 9.** Variation of conductivity with frequency for different volume fraction of Ag in BZN +2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites sintered at 850°C/2hrs.

**Fig. 10.** Variation of dielectric constant with frequency for different volume fraction of Ag in BZN +2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites sintered at 850°C/2hrs and (b) Variation of dielectric constant with frequency at 0.14-volume fraction of silver.



**Fig. 1.** XRD patterns of (a) BZN+2wt% B<sub>2</sub>O<sub>3</sub>, (b) BZN+2wt% B<sub>2</sub>O<sub>3</sub> + 0.1Vf of Ag ,(c) BZN+2wt% B<sub>2</sub>O<sub>3</sub> +0.15Vf of Ag and (d) BZN+2wt% B<sub>2</sub>O<sub>3</sub> +0.18Vf of Ag in BZN-Ag composites sintered at 850°C/2hrs.



**Fig. 2.** Variation of percentage density with sintering temperature of BZN, BZN+B<sub>2</sub>O<sub>3</sub> and BZN+B<sub>2</sub>O<sub>3</sub> +0.15 Ag.

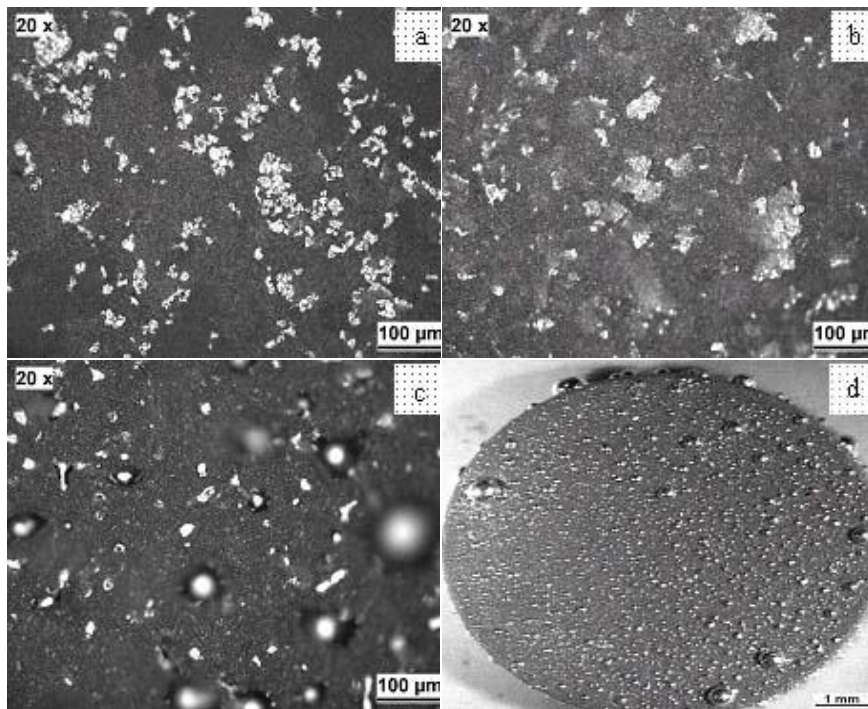


Fig. 3. The optical micrograph of unpolished BZN + 2wt%  $B_2O_3$  + 0.15 Vf of Ag sintered at (a) 850 °C, (b) 900 °C, (c) 950 °C and (d) 975 °C/2hrs .

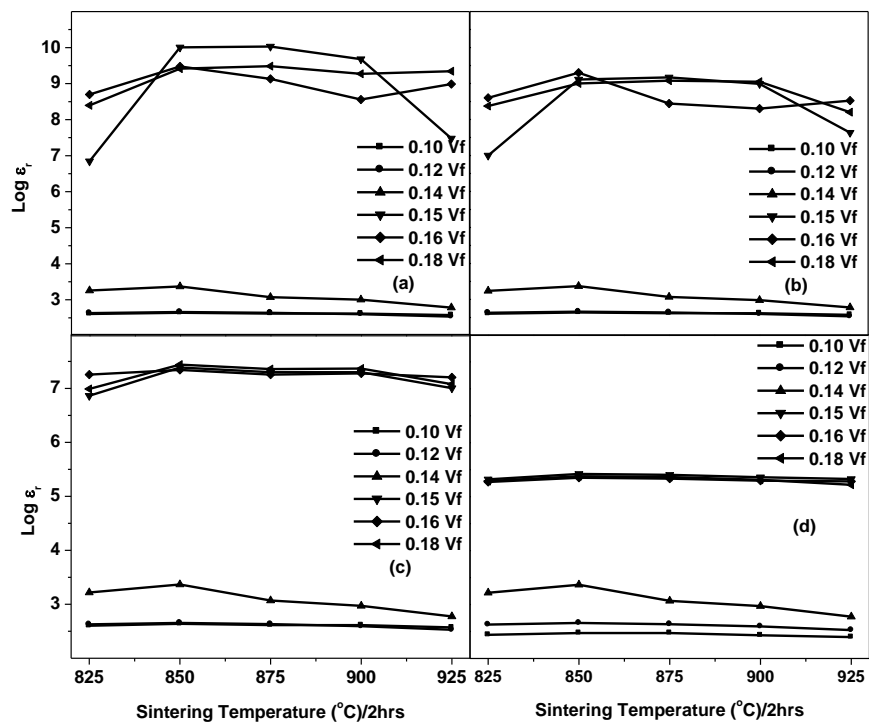
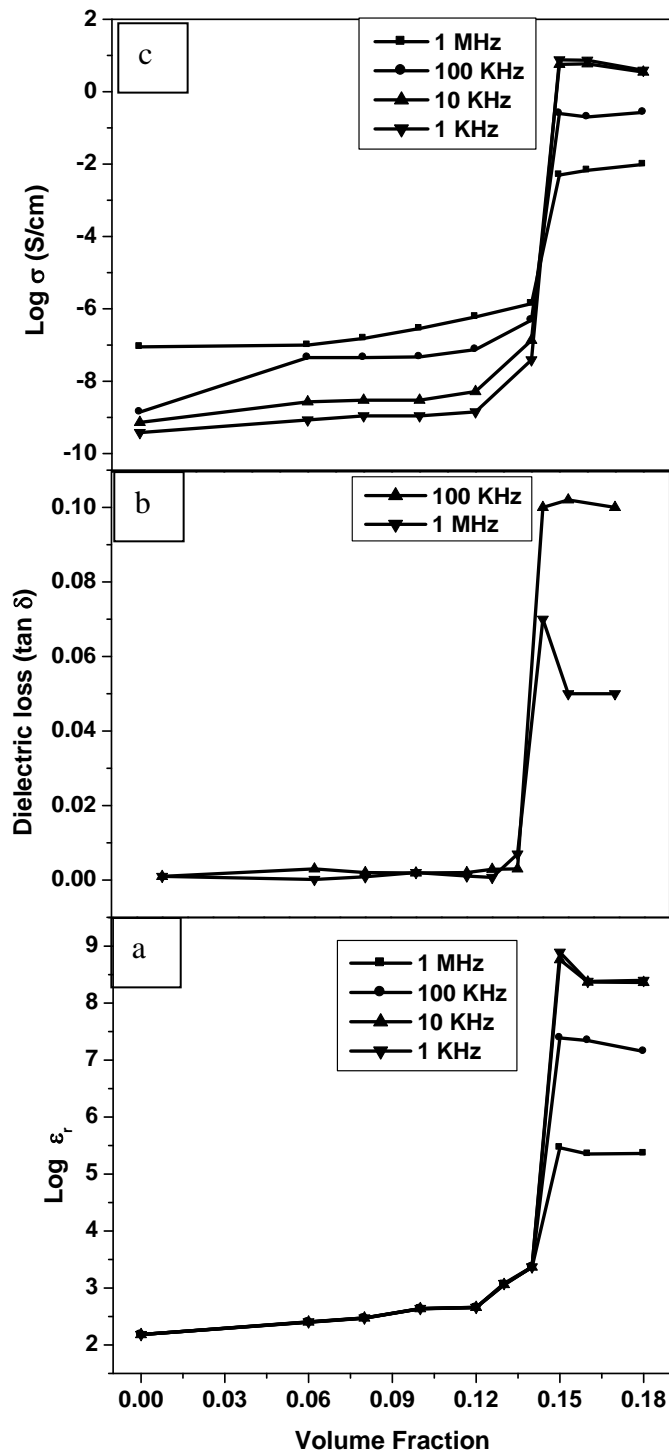


Fig. 4. Variation of dielectric constant of BZN + 2wt%  $B_2O_3$  + Ag with sintering temperature for different volume fraction of silver at (a) 1 KHz, (b) 10 KHz, (c) 100 KHz and (d) 1 MHz.



**Fig. 5.** The variation of (a) dielectric constant, (b) dielectric loss and (c) conductivity with different volume fraction of Ag at different frequency in BZN +2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites sintered at 850°C/2hrs.

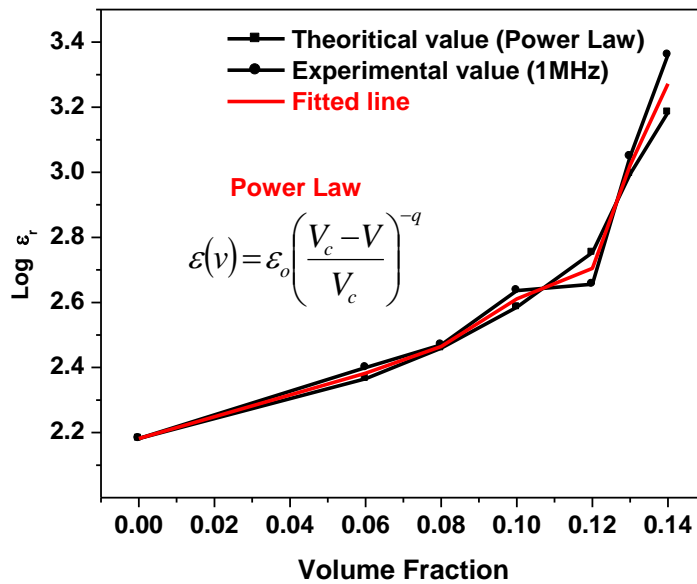


Fig. 6. Variation of dielectric constant of BZN +2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites with different volume fraction of silver below percolation threshold sintered at 850°C/2hrs and the comparison with power law.

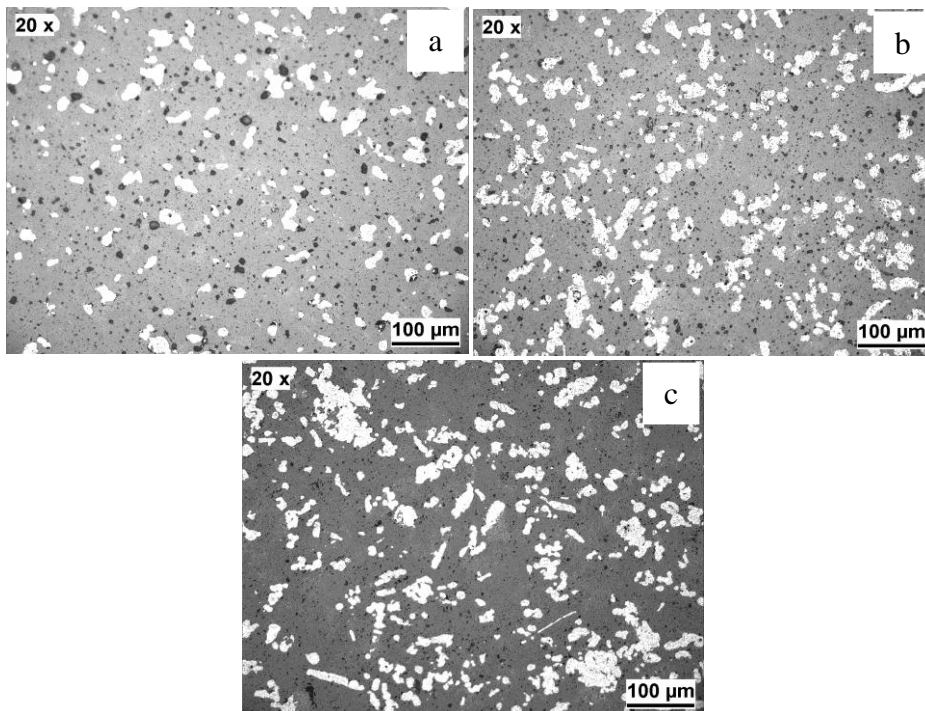
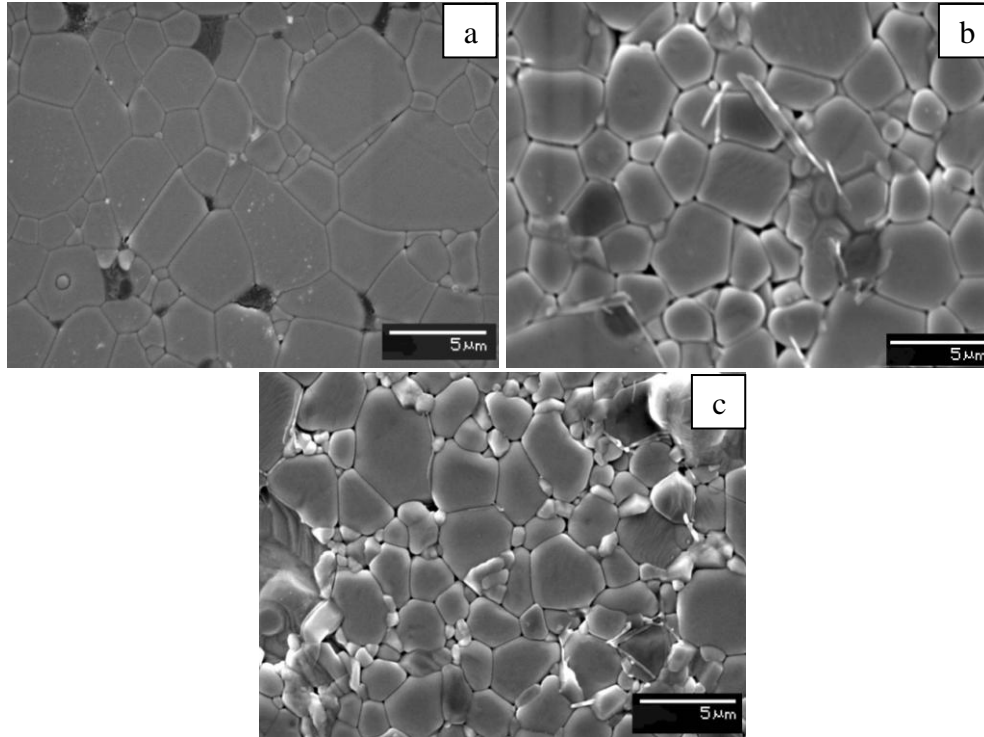
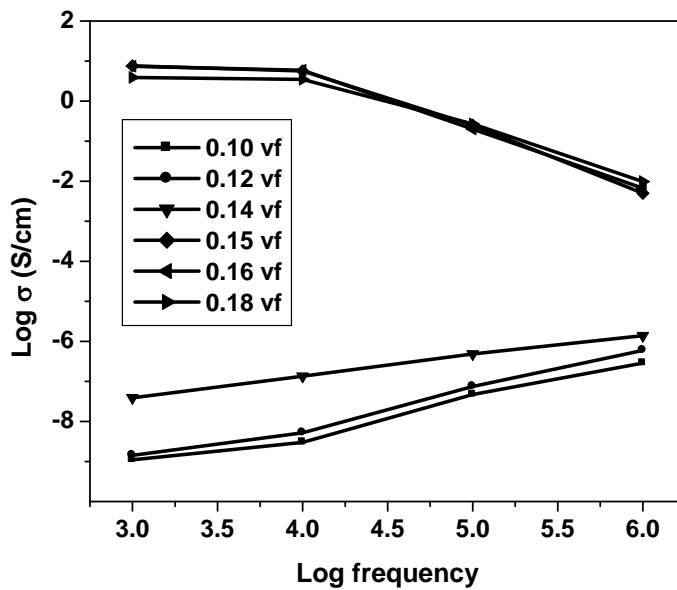


Fig. 7. The optical micrograph of BZN +2wt% B<sub>2</sub>O<sub>3</sub>+ (a) 0.10 Vf of Ag, (b) 0.15 Vf of Ag and (c) 0.18 Vf of Ag composites sintered at 850°C /2hrs.

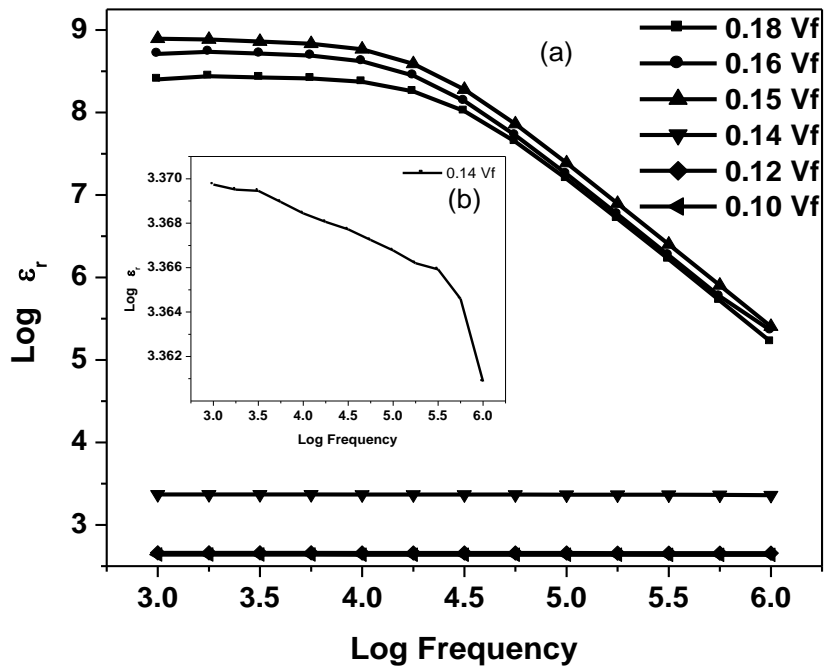


**Fig. 8.** The scanning electron micrographs of (a) BZN +2wt% B<sub>2</sub>O<sub>3</sub>, (b) BZN +2wt% B<sub>2</sub>O<sub>3</sub>+0.10 Vf of Ag and (c) BZN +2wt% B<sub>2</sub>O<sub>3</sub> +0.15 Vf of Ag composites sintered at 850°C/2hrs.



**Fig. 9.** Variation of conductivity with frequency for different volume fraction of Ag in BZN +2wt% B<sub>2</sub>O<sub>3</sub>+Ag composites sintered at 850°C/2hrs.





**Fig. 10.** Variation of dielectric constant with frequency for different volume fraction of Ag in BZN +2wt% B<sub>2</sub>O<sub>3</sub> +Ag composites sintered at 850°C/2hrs and (b) Variation of dielectric constant with frequency at 0.14-Vf of silver.