Development of low permittivity material using fly ash

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Dielectric behaviour of fly ash, barium titanate and three composites of fly ash and barium titanate have been measured in the temperature range 30-200°C and frequency range 100 Hz – 1 MHz. It is observed that dielectric constant of fly ash and composite is low as compared to barium titanate. Moreover, the dielectric constant of fly ash and composites is independent of temperature in the entire range of temperature measurement. It is found that the experimental values of dielectric constant of the composites are in agreement with theoretical value calculated using logarithmic mixing rule given by Linchenecker for determination of effective dielectric constant of the composite.

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Fly ash (FA) is a useful byproduct generated from coal fired thermal power stations. In India maximum power generating plants are coal based. About 70% of India’s annual coal production is used in power generating plants. Which per year produces more than 90 million tons of coal ash as waste material. The production of fly ash by these thermal power plants may cross over 100 million tons in this decade1,2. The disposal of fly ash and bottom ash are today’s burning problems as they have been considered as serious operational constraint and environmental health hazard. Literature survey on fly ash shows that it has been mainly used for construction of building materials and land filling3. Fly ash was utilized in the production of ceramic water filter candle4. For recycling and exploitation of coal fly ash, several approaches have been taken to develop glass-ceramic from fly ash5-7. In spite of all the efforts put in, the consumption of fly ash in these activities is very low as compared to the amount of fly ash being produced in the country, therefore one has to explore other avenue for the proper utilization of fly ash.

Fly ash, a waste material, has various useful compounds and elements. It is reported that fly ash generally contains elements like Cu, Pb, Cd, Ag, Mo, Fe, Ti, Na, Mn, S, P, Zn, and Cl in different concentrations which depend upon the variety of coal used. It has maximum percentage of insulating and semiconducting materials8-10, therefore one can explore the possibility of using fly ash for making electronic devices which are based on insulators and semiconducting materials. The dielectric properties and d.c. resistivity of fly ash in the temperature range 300-500°C have been studied to test the potentiality of fly ash as dielectric material for capacitor application11,12. In this paper, dielectric behaviour of fly ash (of sintered pellet) has been measured in the temperature range 30-200°C and frequency range 100 Hz-1 MHz. In order to compare the dielectric behaviour of fly ash with well-known capacitor material, barium titanate, dielectric behaviour of barium titanate (synthesized in our laboratory) has been studied in the same temperature range. The dielectric behaviour of composites of fly ash and barium titanate has also been reported in the same temperature and frequency range.

Experimental Procedure

The fly ash used in this work was collected from Koradi Thermal Power Station, Near Nagpur, India. Barium titanate, BaTiO3 has been synthesized by conventional solid state ceramic route. In this method, equimolar BaCO3 and TiO2 were mixed in an agate mortar using acetone as mixing media. The mixture was dried at 110°C overnight and dried mixture was calcined at 900°C for 6 h in a porcelain crucible. The calcined powder was pelletized using a hydraulic press at an optimum load of 3 tons. The pellets were sintered at 1050°C for 6 h. In order to improve homogeneity and density, process of sintering was repeated twice. For dielectric measurements, the powder of fly ash was pressed in form of pellet using a die-punch of 9 mm diameter with the help of hydraulic press. The pellets were sintered at 1050°C.
for 6h in order to make dense body for easy handling. Three composites of barium titanate and fly ash were prepared by varying the weight percentage of barium titanate and fly ash. Weight percent of fly ash and barium titanate for composites are given in Table 1. Known amounts of barium titanate and fly ash were mixed in agate mortar in acetone medium to get homogeneous mixture. The mixture was pelleted using hydraulic press at load of 3 tons. Thereafter, the pellets were sintered at 1050°C for 6 h. Henceforth, these five samples fly ash, barium titanate and three composites are refereed by code name FA, BT, FB82, FB64 and FB28 (Table 1).

The X-ray diffraction pattern of powder of finally sintered pellets of all the samples were recorded using Philips (Model PW 1399/00) X-ray diffractometer using CuKα radiations (wave length 1.54064 Å). Morphology of fly ash and composite, FB64 were investigated using Philips (SEM 515) scanning electron microscope. For microstructural characterization, freshly fractured surfaces of sintered pellets were electroded with gold using sputtering method.

For dielectric measurements sintered pellets of all the samples were polished. The polished pellets were electroded by applying silver paint and baking at 400°C for one hour. The electroded pellets were loaded in a locally fabricated sample holder. The capacitance and dissipation factor were measured using HP 4192A LF Impedance Analyser. These measurements were carried out in the temperature range 30-200°C and frequency range 100Hz-1MHz. The temperature of the furnace was controlled using Century System programmable temperature controller (Model CS-7594) having an accuracy ±1°C.

**Results and Discussion**

The X-ray diffraction pattern of all the samples is shown in Fig.1. XRD pattern of barium titanate synthesized in this work has been compared with JCPDS file of barium titanate (no. 5-626). All the peaks observed in the pattern correspond to barium titanate, which ruled out presence of second phase or unreacted compounds (of BaCO3 and TiO2). A good agreement with observed and JCPDS values of ‘d’ spacing for different planes confirmed the formation of barium titanate. Using XRD data the value of lattice parameters for tetragonal barium titanate are calculated and found as a = 3.96Å and c = 4.03Å. The sharp peaks in the XRD pattern of fly ash are due to presence of crystalline phases quartz and mullite. The XRD pattern of all the composites revealed presence of both the materials, i.e., barium titanate and fly ash. Peaks observed in the patterns are either of barium titanate or fly ash. No new peak due to reaction between barium titanate and fly ash has been observed. On comparing XRD patterns of the composites with XRD pattern of barium titanate it is

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**Table 1—Weight per cent, bulk density and volume fraction of the samples**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample Code</th>
<th>Fly Ash (wt.%)</th>
<th>BaTiO3 (wt %)</th>
<th>Bulk Density (g/cm³)</th>
<th>Volume Fraction of FA (v₁)</th>
<th>Volume Fraction of BT (v₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FA</td>
<td>100</td>
<td>0</td>
<td>1.42</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>FB82</td>
<td>80</td>
<td>20</td>
<td>1.92</td>
<td>0.93</td>
<td>0.07</td>
</tr>
<tr>
<td>3</td>
<td>FB64</td>
<td>60</td>
<td>40</td>
<td>2.24</td>
<td>0.84</td>
<td>0.16</td>
</tr>
<tr>
<td>4</td>
<td>FB28</td>
<td>20</td>
<td>80</td>
<td>3.12</td>
<td>0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>BT</td>
<td>0</td>
<td>100</td>
<td>5.10</td>
<td>0.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Note—These five samples: fly ash, barium titanate and three composites are denoted by abbreviated name FA, BT, FB82, FB64 and FB28 throughout the text.
noticed that the strongest peak of barium titanate (2θ = 31.46°) is shifting towards lower angle as fly ash content increases in composite. The increase in ‘d’ values leads to increase in value of lattice parameters ‘a’ or ‘c’. The increase in lattice parameters may be due to the occupancy of bigger size ions from fly ash at Ba or Ti sites in BaTiO₃.

To get dense barium titanate, sintering temperature required ≥ 1300°C, therefore for calculation of bulk density, theoretical density and porosity are necessary. Bulk density (dₙ) of the material is given by total weight of the pellet divided by total volume of the pellet. True density or theoretical density (dₜh) is given as molecular weight of the sample divided by volume of its unit cell. The % porosity of the barium titanate was calculated using formula:

% porosity = [(dₜh - dₙ)/(dₜh)]×100  …(1)

Bulk density (dₙ) of all the samples namely FA, BT, FB82, FB64 and FB28 were calculated as mentioned above and given in Table 1. Theoretical density (dₜh) of barium titanate has been calculated from molecular weight of the barium titanate divided by volume of its unit cell. The percentage porosity was calculated using Eq. (1) and found to be approximately 16. Low density of barium titanate synthesized in this work compared to density reported in the literature is due to low sintering temperature used for synthesis of barium titanate.

Scanning electron micrographs (SEM) of the samples FA and FB64 are shown in Figs 2 (a) and (b), respectively. Fig. 2a reveals that morphology of fly ash particles is spherical. Moreover, grain size distribution is also small. Average grain size of fly ash is ≈ 3 μm. The scanning electron micrograph of sample FB64 (60 wt.% of fly ash and 40 wt.% of barium titanate) is shown in Fig. 2b. Micrograph of this sample shows a few grains of larger size as compared to other grains. Since from the Fig. 2a it is observed that grain size of fly ash is ≈ 3 μm, therefore a few grains of larger size ≈ 10 μm may be of barium titanate. Volume fraction of barium titanate in composite FB64 is only 0.16 (Table 1) thus only a few grains of larger size are seen. Ceramic barium titanate have wide differences in grain size depending on exact composition and processing conditions. Generally, barium titanate prepared by solid state method has grain size in range 10-20 μm. But due to low sintering temperature used for synthesis of barium titanate in this work, grain size is ≈ 10 μm.

The variation of dielectric constant (ε) and dissipation factor (D) with temperature of samples BT, FA, FB28, FB64 and FB82 are shown in Figs 3-7, respectively. The experimental values of room temperature dielectric constant and dissipation factor of all the samples are given in Table 2. Table 2 shows that value of dielectric constant increases with increasing concentration of barium titanate in composite.

Figure 3 shows variation of dielectric constant and dissipation factor with temperature at three different frequencies for BaTiO₃. It has been found that as temperature increases, dielectric value increases and a peak in dielectric constant is observed around 128°C, where ferroelectrics to para-electric transition takes place. This temperature is in agreement with transition temperature reported in the literature. The low value of dielectric constant is attributed to low bulk density of barium titanate synthesized for the
Fig. 3—Variation of dielectric constant and dissipation factor with temperature for sample BT.

Fig. 4—Variation of dielectric constant and dissipation factor with temperature for sample FA.

Fig. 5—Variation of dielectric constant and dissipation factor with temperature for sample FB82.

Fig. 6—Variation of dielectric constant and dissipation factor with temperature for sample FB64.
Fig. 7—Variation of dielectric constant and dissipation factor with temperature for sample FB28.

Variation of dielectric constant and dissipation factor with temperature for sample FB28.

The dielectric constant of fly ash is low ($\varepsilon_r \sim 10$) which remains almost constant in the entire range of temperature measurement. The dissipation factor is also low. The low value of dielectric constant and dissipation factor reflects insulating behaviour of fly ash.

Figures 5-7 show the variation of dielectric constant with temperature for samples FB82, FB64 and FB28, respectively. It has been observed that increase in frequency decreases the magnitude of dielectric constant. Dielectric constant of these composites is almost constant in the entire range of temperature measurements. It is observed that dielectric constant of these composites is low as compared to barium titanate. Moreover, there is not any anomaly in the dielectric constant versus temperature plot of composites. The suppression of ferroelectric to paraelectric transition in $\varepsilon_r$ versus $T$ plot of composites may be due to diffusion of iron in barium titanate lattice from fly ash (fly ash has Fe ions in minor amount). It is reported that substitution of even a small amount of iron in barium titanate eliminates the dielectric peak and reduces the value of dielectric constant. The dielectric behaviour of these composites is very similar to dielectric behaviour of glass dispersed barium titanate.

The low value of dielectric constant of composites is explained using logarithmic mixing rule given by Linchtenecker for determination of effective dielectric constant of the composite. The mathematical equation for logarithmic mixing rule is given below:

$$\log K_{\text{effective}} = v_1 \log K_1 + v_2 \log K_2$$  \hspace{1cm} \ldots(2)

where notations $v_1$, $v_2$, $K_1$ and $K_2$, respectively are volume fraction and dielectric constant of the component 1 and 2 present in the composite. In the present work, composites were prepared using wt.% of fly ash and barium titanate. The weight % ratio (Table 1) is converted into volume fraction using bulk density of fly ash and barium titanate (Table 1). The volume fractions of fly ash and barium titanate in different composites are given in Table 1. The effective dielectric constant of the composites is calculated on substituting values of volume fraction and room temperature dielectric constant of fly ash and barium titanate in Eq. (2). The calculated value of dielectric constant of all the composites is given in Table 2. It is observed that experimental and calculated values of dielectric constant of the composites are in agreement within experimental error.

**Conclusions**

X-ray diffraction of composites shows that there is not any reaction between barium titanate and fly ash up to 1050°C (max. sintering temperature used in this work). Dielectric constant of fly ash increases with increasing weight % of barium titanate in composites. With the change in dielectric constant value of fly ash from 10 to 25, its utility classification undergoes a sea change that is from insulator to capacitor. The variation of dielectric constant of composites is

<table>
<thead>
<tr>
<th>Samples code</th>
<th>Dielectric constant ($\varepsilon$) at RT</th>
<th>Dielectric constant calculated using Eq. (2)</th>
<th>Dissipation factor ($D$) at RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>10</td>
<td>—</td>
<td>0.009</td>
</tr>
<tr>
<td>FB82</td>
<td>15</td>
<td>16</td>
<td>0.010</td>
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<tr>
<td>FB64</td>
<td>20</td>
<td>25</td>
<td>0.025</td>
</tr>
<tr>
<td>FB28</td>
<td>80</td>
<td>100</td>
<td>0.050</td>
</tr>
<tr>
<td>BT</td>
<td>920</td>
<td>—</td>
<td>0.100</td>
</tr>
</tbody>
</table>
almost independent of temperature. Hence, they can be a potential candidate for thermally stable capacitor. A thorough chemical analysis of the used fly ash is required for understanding the role of the various constituents present in the fly ash in making a reliable composite dielectric material.

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References
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