Synthesis, characterization and dielectric study of PbZrO$_3$ and BaZrO$_3$

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ABSTRACT
Solid solution of the Perovskites PbZrO$_3$ and BaZrO$_3$ were synthesized by solid state reaction technique. These compounds have been characterized by XRD, differential thermal analysis (DTA), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). The XRD pattern obtained on these powders show the formation of pure orthorhombic phase of PbZrO$_3$ and BaZrO$_3$ without any impurities. The dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and quality factor (Q) of the compounds have been studied at 1 kHz in the temperature range of 300K to 1150K. The dielectric constant of PbZrO$_3$ and BaZrO$_3$ show rapid increase above 700K and 820K respectively. The dielectric loss show similar behaviour as dielectric constant.

Keywords: Dielectric constant ($\varepsilon'$), Dielectric loss ($\varepsilon''$), XRD, DTG, PbZrO$_3$ and BaZrO$_3$.

INTRODUCTION
Dielectric materials are widely used in wireless communication devices. These require a high dielectric constant and low dielectric loss [1]. Lead Zirconate (PbZrO$_3$) and Barium Zirconate (BaZrO$_3$) are ABO$_3$ perovskite dielectric material that is both chemically and mechanically stable. They have unique dielectric properties that make them suitable for digital actuators and high charge storage capacitors [2]. PbZrO$_3$ based antiferroelectric materials have been extensively studied over the past several decades for application as high-energy storage capacitors and high strain actuators/ transducers [3-9]. More recently, with the development of microelectronic devices, antiferroelectric materials have been explored for applications such as microactuators in microelectromechanical systems (MEMS) and decoupling capacitors in high speed Dynamic Random Access memory (DRAM) devices [10-11].

In this work, we describe the synthesis characterization and dielectric properties of PbZrO$_3$ and BaZrO$_3$. 

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MATERIALS AND METHODS

Sample Preparation:
Polycrystalline samples of PbZrO$_3$ and BaZrO$_3$ compounds were synthesized by the solid state reaction technique, using high purity (99.99% pure) powders of BaO, PbO and ZrO$_2$, procured from Alfa Aesar, A Johnson Mathey, Chemical India Pvt. Ltd. The stoichiometric mixture of these oxides were mixed and heated in alumina crucible at temperature 1300K for 50 hrs. In this process the mixture was followed by one intermediate grinding and the final product was cool down slowly.

XRD, DTA, TGA and DTG Measurement:
The X-ray diffraction of the compound was studied using x-ray diffractometer (Thermoelectron-XRL EXTRA) at room temperature by using CuK$_\alpha$ radiation with $\lambda$=0.15418nm in a wide range of Bragg angle ($10^0$≤$2\theta$≤$90^0$).

DTA, TGA and DTG studies of the compounds were carried out in nitrogen gas using a thermal analyzer (PERKIN ELEMER PYRIS) at a heating rate of 283K/min and flow rate of 100ml/min from 323K to 1123K.

Dielectric Measurement:
The compounds were pressed at a pressure of 7.19x10$^8$ Nm$^{-2}$ to form pellets of circular cross section (area~0.90x10$^{-4}$m$^2$ and thickness~ 0.30x10$^{-2}$m). The pellets were then sintered in air for 28hrs at 1500K. The pellet covered with film of silver paint on the opposite surfaces to obtain a good contact was inserted between the two silver electrodes. A LCR-Q meter (model-928, Systronic, India) was used to measure the capacitance(C) and quality factor(Q) of the sample at different temperatures and at a frequency of 1kHz. The dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of the sample was calculated by using the following relations [12-13]

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$  \hspace{1cm} (1)

$$\varepsilon'' = \frac{\varepsilon'}{Q}$$  \hspace{1cm} (2)

where C = the capacitance of the capacitor in Farad, d= thickness, A= face area of the pellet, $\varepsilon_0$ = the permittivity of free space and Q= quality factor respectively.

RESULT AND DISCUSSION

The XRD pattern of PbZrO$_3$ and BaZrO$_3$ are shown in Figs. (1-2). From XRD pattern, $d_{hkl}$ planes have been evaluated using relation [14].

$$d_{hkl} = \frac{0.15418}{2\sin \theta}$$  \hspace{1cm} (3)
From these \( d_{hkl} \) planes, structures of the studied compounds were resolved using usual procedure. All the peaks have been assigned with proper hkl values. This confirms that the prepared compounds has single phase and no unreacted part of the starting material was left. The unit cell parameters are given in table1.
FIG 3  DTA, TGA and DTG trace of BaZrO₃

FIG 4  DTA, TGA, DTG trace of PbZrO₃
Table 1: Structural parameters of orthorhombic unit cell, calculated density ($d_0$), density of pressed pellets ($d_p$) and values of pore fraction ($f_p$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit cell</th>
<th>Lattice parameter</th>
<th>Density $d_0$ ($\text{kgm}^{-3} \times 10^3$)</th>
<th>Density $d_p$</th>
<th>Pore fraction $f_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZrO$_3$</td>
<td>Orthorhombic</td>
<td>$a_0$ 0.68262, $b_0$ 1.04412, $c_0$ 0.58922</td>
<td>4.38</td>
<td>4.25</td>
<td>0.028</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td>Orthorhombic</td>
<td>$a_0$ 0.67587, $b_0$ 1.16347, $c_0$ 0.56352</td>
<td>5.19</td>
<td>5.02</td>
<td>0.033</td>
</tr>
</tbody>
</table>

The DTA, TGA and DTG trace of studied Zirconate are shown in Figs. (3,4). DTA trace of both zirconate show a broad peak around ~ 400K which is indicative of exothermic reaction.

TGA trace show weight loss in two successive steps. The weight loss and temperature region is shown in table-2 for both Zirconate.

Table 2: Percentage of weight loss calculated from TGA trace for studied Zirconates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. region (K)</th>
<th>Percentage of weight loss in the I$^\text{st}$ step</th>
<th>Temp. region (K)</th>
<th>Percentage of weight loss in the II$^\text{nd}$ step</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZrO$_3$</td>
<td>323-573</td>
<td>0.90 (%)</td>
<td>573-748</td>
<td>1.60 (%)</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td>323-558</td>
<td>1.03 (%)</td>
<td>558-673</td>
<td>2.13 (%)</td>
</tr>
</tbody>
</table>

The weight loss completed at 748K and 673K in BaZrO$_3$ and PbZrO$_3$ respectively. Such a small loss in weight is due to removal of absorbed water and other gaseous species. No further weight loss appear over higher temperature which indicates that the compounds are stable and do not show decomposition up to 1123.

The DTG trace of BaZrO$_3$ and PbZrO$_3$ show maximum rate of mass change at 608K and 538K respectively. The variation of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) and quality factor (Q) with temperature at 1 kHz is shown in Figs (5-6).

It is seen that these compounds have dielectric constant 25 and 39 for BaZrO$_3$ and PbZrO$_3$ at 400K respectively. Since dielectric constant ($\varepsilon'$) seems to have almost no temperature dependence, these values may be taken as the room temperature value of the materials. The reported value of $\varepsilon'$ has been calculated using the capacitance of the pressed pellets. The density of these pellets remains less than theoretical density. This means pellet contains air pores. Therefore a correction for pore fraction ($f_p$) is essential to obtain the bulk value of dielectric constant ($\varepsilon_b$) and is given by [15].

$$f_p = \frac{d_o - d_p}{d_o}$$

For low conducting solids $\varepsilon'$ and $f_p$ are related by the relation [16].

$$\varepsilon_b = \frac{(\varepsilon' - f_p)^3}{1-f_p}$$

The evaluated value of $\varepsilon_b$, $\varepsilon'$ are 25 and 288 for BaZrO$_3$ and PbZrO$_3$ respectively. The value of $\varepsilon'$ becomes large as temperature is increased and validity of eq. (5) becomes doubtful. Further
this formula change only the magnitude of $\varepsilon'$ but not the nature of variation of $\varepsilon'$ with temperature. Therefore we have not used this correction at higher temperature.

The values of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of these compounds at different temperature and at frequency 1kHz are given in table 3 and 4 respectively.

Table-3 The dielectric constant ($\varepsilon'$) for studied Zirconate at different temperature

<table>
<thead>
<tr>
<th>Compound</th>
<th>400K</th>
<th>600K</th>
<th>800K</th>
<th>1000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZrO$_3$</td>
<td>25</td>
<td>39</td>
<td>61</td>
<td>1.12x10$^3$</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td>3.98x10$^2$</td>
<td>6.3x10$^2$</td>
<td>2.50x10$^3$</td>
<td>3.98x10$^6$</td>
</tr>
</tbody>
</table>

Table-4 The dielectric loss ($\varepsilon''$) for studied Zirconate at different temperature

<table>
<thead>
<tr>
<th>Compound</th>
<th>400K</th>
<th>600K</th>
<th>800K</th>
<th>1000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZrO$_3$</td>
<td>2</td>
<td>3</td>
<td>1.58x10$^7$</td>
<td>2.00x10$^3$</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td>11</td>
<td>45</td>
<td>2.24x10$^4$</td>
<td>8.90x10$^7$</td>
</tr>
</tbody>
</table>

It is seen from table 3 and 4 that the systematic trend of $\varepsilon'$ and $\varepsilon''$ variation reveals that polarization mechanism in all these Zirconate is same. A relatively larger value of $\varepsilon'$ in case of PbZrO$_3$ appears due to the presence of chemical impurities which forms some kind of donor centers and has larger polarizability. The dielectric constant has very slow increase at lower temperature. This shows that there is no chance for the existence of thermally generated charge carriers at lower side of temperature. The lower value of $\varepsilon'$ below 600K indicates that free charge carriers generated from impurities is also small. Well made electrode rules out the chance of interfacial polarization. Therefore this slow increase seems to be the combined effect of lattice and electronic polarizabilities of individual ions. The increase of these polarizabilities seems to compensate the slight decrease of polarizability due to decrease in the number of ions per unit volume following the lattice expansion with temperature. However, it must be noticed that the increase of $\varepsilon'$ with T is very small in comparison to the variation one expects for ionic solids. This indicates that either thermal expansion of these compounds is very small or they have some other kind of polarization mechanism.

The dielectric constant ($\varepsilon'$) of these compounds have much faster increase above certain critical temperature ($T_k$). The dielectric loss ($\varepsilon''$) shows similar behaviour above $T_k$. The critical temperature ($T_k$) is 820K and 700K for BaZrO$_3$ and PbZrO$_3$ respectively. The faster increase in dielectric constant ($\varepsilon'$) above $T_k$ is due to space charge polarization [17,18]. The pressed sample develops a considerable amount of space charge polarization arising out from the defects or impurities present in the bulk or at the surface of the material.
FIG. 5 Plot of dielectric constant (log $\varepsilon'$), dielectric loss (log $\varepsilon''$) and quality factor (Q) against absolute temperature (T) for BaZrO$_3$.

FIG. 6 Plot of dielectric constant (log $\varepsilon'$), dielectric loss (log $\varepsilon''$) and quality factor (Q) against absolute temperature (T) for PbZrO$_3$. 

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CONCLUSION

The XRD studies confirm that the studied compounds have single phase orthorhombic structure at room temperature. DTA, TGA and DTG studies show that the compounds are stable above certain temperature. The dielectric constant and loss have very slow increase up to $T_k$. Above $T_k$ this increase becomes much faster. The value of $T_k$ is different for both compounds. The reason for faster increase of $\epsilon'$ and $\epsilon''$ above $T_k$ is due to space charge effect of thermally generated charge carriers.

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REFERENCES