Frequency dependence impedance study of polymer ceramic composite thick film

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Abstract

Thick film has been prepared using as synthesized BaZr$_{0.1}$Ti$_{0.9}$O$_3$ (BZT) ceramic and polyvinyl alcohol by hot press technique. Phase formation of synthesized BZT ceramic is confirmed by X-Ray diffraction and dispersion of ceramic in a polymer matrix of the thick film is observed by Scanning electron microscopy. Finally, an electrical property of the thick film is studied by using impedance spectroscopy. Temperature dependence dielectric study shows the increment of dielectric constant with temperature. Frequency dependence impedance and modulus has been studied for different temperatures and it indicates the Non-Debye nature and temperature dependence relaxation time. Nquist plot of impedance observed the presence of grain and grain boundary and their parameters has been evaluated by using electrical equivalent circuits. AC conductivity datas are well agreed with the impedance plot and its response the Jonscher’s power law. DC conductivities are extracted from the power law fitting of AC conductivity and activation energy has been calculated.
Introduction

Polymer composites have received significant attention over the past 30 years due to widespread applications for the development of functional materials to fulfill the requirements of cheap, reliable, durable and most of all environmentally-friendly batteries which is necessary for the most efficient energy storage and conversion device applications. Polymer matrices with embedded inorganic fillers, nanoparticles or clusters are particularly appealing for optical, electronic, dielectric and magnetic applications. In particular, the development of hybrid layers with tailored dielectric properties represents a key issue in many technological fields.

The AC electrical studies of the polymers reveal some structural details and add valuable complementary information to electrical application of polymer materials. The contribution of polymer such as grain (bulk), grain boundaries and the electrode effects are able to identify in the frequency dependent measurements and also it can supply the valuable information with microstructural details to electrical applications of polymer materials.

Preparation

Ceramics powder $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ (BZT) $\Rightarrow$ Solid State Route
Polymer composites PVA:BZT $\Rightarrow$ Ceramic powder mixed in aqueous solution of PVA by volume ratio 25:75
Thick film $\Rightarrow$ Hot press technique (at 100°C for 3 mins under 300MPa)
XRD spectrum of BZT ceramic powder

Single phase perovskite structure
JCPDS no. 36-0019
Centro symmetric position due to larger ionic radii and stable of Zr$^{4+}$ than Ti$^{4+}$

SEM image of PVA:BZT thick film

Homogeneous distribution with some agglomeration
Porous free
Frequency dependence dielectric study

\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + \omega^2 \tau^2} \]

Shift towards higher frequency – Thermally activated relaxation phenomenon

Low frequency anomaly – due to space charge polarization
Impedance Spectroscopy

Equivalent circuit

Depressed semicircle indicates non-Debye nature

Constant phase element (CPE)

\[ Z_{CPE} = \left[ Q(j\omega)^{\alpha} \right]^{-1} \]
Frequency dependence of Modulus spectrum

- Modulus spectrum neglects the space charge polarization and highlights the bulk property.

Combined plot of $M''$ and $Z''$

- $M''$ spectrum highlights the higher capacitance value (grain capacitance at high frequency) and $Z''$ spectrum highlights the higher resistance value (grain boundary resistance at low frequency).
### Parameters obtained from Nquist plot

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<th>Temperature °C</th>
<th>Rg (MΩ)</th>
<th>Cg (pF)</th>
<th>n</th>
<th>Rgb (MΩ)</th>
<th>Cgb (pF)</th>
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Resistance of grain and grain boundary decreases with temperature – NTCR behavior

Variation of grain capacitance are more compared than grain boundary capacitance – highlighted in modulus plot
AC conductivity spectrum

Jonscher’s power law

\[ \sigma_{ac} = \sigma_{dc} + A\omega^n \]

- \( A \) – temperature dependent pre-exponential factor
- \( n \) – the degree of interaction between mobile ions and lattices

Increment of segmental chain motion in polymer and charge carriers in ceramic enhances the conductivity at high temperature.
Activation energy – Arrhenius plot

Arrhenius law,

\[ \sigma_{dc} = \sigma_o \exp \left( \frac{E_a}{KT} \right) \]

\[ f_{max} = f_o \exp \left( \frac{E_a}{KT} \right) \]

Relaxation process does not govern the conduction mechanism

Lower activation energy indicates the contribution of all charge carriers in conduction mechanism but they may not contribute to the relaxation process
Conclusion

In summary, polymer composites of PVA with BaZr$_{0.1}$Ti$_{0.9}$O$_3$ have been prepared and the frequency dependent dielectric, impedance, modulus and AC conductivity have been studied. Phase analysis shows that the single perovskite structure of ceramics and morphological study shows that the homogenous distribution of filler in polymer matrix. Dielectric and modulus spectrum confirms the relaxation process arises due to the segmental chain in polymer and dipoles in ceramics. Complex impedance spectrum shows the two relaxation and conduction mechanism due to the effect of grain and grain boundary present. The conduction mechanism of complex impedance spectrum supports the ac conductivity and ac conductivity follows the Jonscher’s power law. Lower activation energy indicates the contribution of all charge carriers in conduction mechanism but they may not contribute to the relaxation process. This kind of interfaced materials can show the better property in scientific and industrial applications.
Reference