Abstract of Contribution 171521

Friday, 23/Jun/2017 12:45pm - 1:00pm
ID: 171521 / S-12: 5
S) Spintronics and Magnetic Materials
Oral
Topics: Multiferroics
Keywords: magnetoelectric composites, Phase stability, magnetodielectric property

Electrical and Magnetic Behavior of Magnetoelectric BaTiO3-NiFe2O4 Composites: Effect of Phase Connectivity of the Constituent Phases

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The research on magnetoelectric composites has been fueled up by their potential applications in microwave devices, sensors, transducers, information storage, spintronics and multiple-state memories. In the present work, ferroelectric BaTiO$_3$ (BT) - ferromagnetic NiFe$_2$O$_4$ (NF) composites were prepared by different powder synthesis route namely solid-state, auto-combustion, and hybrid precipitation to tailor the phase connectivity of the constituent phases. Functional properties (dielectric, piezoelectric, magnetic, magnetodielectric and magnetoelectric) of BT-NF composite thus prepared were studied as a function of NF content in the BT matrix in the range 20-60 mole% as well as the connectivity of the constituent phases. X-Ray diffraction (XRD) studies on sintered (1200 °C/4hr) composites indicates good chemical compatibility of the constituent phases. Microstructural (SEM) study revealed that the powder synthesis technique and the composition of the ferrite phase has a strong influence on the connectivity of the constituent phases. Frequency and temperature dependent dielectric behaviour study confirm the existence of conductivity relaxation in the composite and the constituent phase connectivity have a significant influence on it. The ferroelectric and magnetic behaviour of the composite could be well predicted from the consideration of dilution effect observed in composites materials. Composite properties (magnetocapacitance and magnetoelectric (ME) voltage coefficient) were found to be dependent both on the relative amount of constituent phases, the chemical composition of the ferrite phase and the connectivity of the constituent phases. The highest ME coefficients 1.21 mV.cm$^{-1}$.Oe$^{-1}$ was obtained for BT-NF 70:30 composites prepared by hybrid precipitation route. The study suggests that the BT-NF composite prepared by hybrid precipitation technique have the potential for multifunctional application.
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Ferroelectric- Ferromagnetic Composites

Enhanced magnetodielectric effects
Adequate magnetoelectric properties

indirect coupling — strain mediated

Material aspects

1. Magnetic properties of the ferromagnetic phase
   Magnetostriction
   Magnetoresistance

2. Dielectric - piezoelectric properties of ferroelectric phase
   Relative permittivity ($\varepsilon_r$)
   Loss tangent (tan $\delta$)
   Piezoelectric constant ($d_{33}$)

Processing aspects

- Size, shape and distribution of the constituent phases
- Chemical-thermal-mechanical compatibility of the phases
- Presence of third phase if any (pores, impurity)
OBJECTIVE

Material System explored

BaTiO$_3$-NiFe$_2$O$_4$ (BT-NF)

Specific scope

✓ Effect of constituent phases on the functional properties of the BT-NF composites

✓ Study the distribution of constituent phases tailored by powder synthesis techniques
Solid-state processing

\[
\begin{align*}
\text{BaCO}_3 & \quad \text{TiO}_2 \\
\downarrow \text{Mixing} & \quad \downarrow \text{Mixing} \\
\downarrow \text{Calcination} (1000^\circ\text{C}/4\text{hr}) & \quad \downarrow \text{Calcination} (900^\circ\text{C}/4\text{hr}) \\
\text{Calcined powder} (\text{light yellow}) & \quad \text{Calcined powder} (\text{black}) \\
\downarrow \text{Pulverization 6hr} & \quad \downarrow \text{Pulverization 6hr} \\
\text{BaTiO}_3 (\text{BT}) & \quad \text{NiFe}_2\text{O}_4 (\text{NF}) \\
\downarrow \text{Mixing/6hr} & \quad \downarrow \\
\text{BT+NF (in mole ratio)} & \quad \\{40-60; 50-50; 60-40; 70-30; 80-20\}
\end{align*}
\]

Auto-combustion

\[
\begin{align*}
\text{Ba(NO}_3\text{)}_2 & \quad \text{Fe(NO}_3\text{)}_3 & \quad \text{Ni(NO}_3\text{)}_2 \\
\downarrow \text{Mixing} & \quad \downarrow \\
\downarrow \text{Precursor solution} & \quad \downarrow \\
(\text{Hot plate with magnetic stirrer}) & \quad \\
\downarrow \text{Thick citrate sol} & \quad \downarrow \\
\downarrow \text{Citrate gel} & \quad \\
\downarrow \text{Combustion residue ash} & \quad \\
\downarrow \text{Calcination} (1000^\circ\text{C}/2\text{hr}) & \quad \\
\downarrow \text{Fine powder} & \quad \\
\end{align*}
\]

Hybrid precipitation

\[
\begin{align*}
\text{BaTiO}_3 \text{ or BT (solid state) powder} & \\
\downarrow \text{Basic suspension} & \quad \text{Co-precipitation} \\
(\text{pH 10 or slightly more}) & \quad \text{On BT powder} \\
(\text{Magnetic Stirrer}) & \quad \text{(light brown)} \\
\downarrow \text{Settled powder at bottom of the glass beaker used} & \quad \downarrow \\
\downarrow \text{Filtration and washing} & \quad \\
\downarrow \text{Air drying} & \quad \text{Filter cake to powder} \\
\downarrow & \quad (\text{BT+hydroxide of Ni and Fe}) \\
\downarrow & \quad \text{Fine powder} \\
\end{align*}
\]

Sample code

- SS BT-NF: (100-x)BT-xNF
  - X = 20, 30, 40, 50 and 60
- AC BT-NF: (100-x)BT-xNF
  - X = 20, 30, 40, 50 and 60
- HP BT-NF: (100-x)BT-xNF
  - X = 20, 30, 40, 50 and 60
RESULTS AND DISCUSSION

Relative amount of constituent phases
Thermochemical compatibility of BT: NF composites

- Peaks are of BT and/or NF phase
- No impurity phases detected
- No reaction between the constituent phases up to 1200 °C
- Analysis of the spectrum confirms the amount of the constituent phases

XRD patterns of sintered at 1200 °C/4hr obtained by hybrid precipitation composite powder

**BT** = BaTiO$_3$, **NF** = NiFe$_2$O$_4$
**Microstructure: Relative amount of phases**

- **HP BT-NF: 80-20**
  - BT phase is well connected in 80-20 and 70-30 but there is a gross loss of connectivity in 50-50 composite.

- **HP BT-NF: 70-30**
  - Spherical shape ➔ BT
  - Pyramidal shape ➔ NF

- **HP BT-NF: 50-50**
  - BT Grain size range: 0.4-0.7μm
  - NF Grain size range: 1.2-1.45 μm
  - The grain size of constituent phases are independent of their relative amount.
- $\varepsilon_r$ increases with increasing ferrite at low $f$ whereas it with decreasing ferrite content at high $f$

- Dielectric dispersion in the low frequency region
  - Maxwell-Wagner polarization
  - Interfacial heterogeneity
  - Electron exchange $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$

- At Higher frequency
  - dilution of permittivity of BT with NF phase

- At high frequency Dielectric loss decreases due to the suppression of domain wall motion.
Temperature dependent dielectric behaviour: Relative amount of phases

- Broad peak in the range 120-140 °C — Ferroelectric-paraelectric Transition
- Peak shift
- Temperature ↑ $\varepsilon_r$ ↑

Hopping of electron $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$

Intrinsic ionic polarization,
Complex impedance Analysis: Relative amount of phases

Non-Debye type relaxation

Modulus plot confirms two different contribution in Conduction process

Impedance decreases with increasing temperature and ferrite content

Conduction process is governed by small polaron hopping
Complex impedance in frequency spectrum: Relative amount of phases

- Peak shifts at higher frequency with increasing temperature
- Dielectric relaxation is thermally activated
- Broadening of peaks
- Presence of immobile species

Position of peaks shifts at right side
- Space charge polarization at grain boundary
Ferroelectric and Magnetic properties: Relative amount of phases

- Lossy Ferroelectric
- Low resistive ferrite phase hinders polarization and thus prevents saturation-low $P_r$ and $P_s$ value
- Magnetic field induced disturbance of dipole alignment causes discontinuity at $E=0$

- Ferromagnetic nature is observed
- Decreased value in saturation magnetization is explained by Bruggeman’s theory
- Calculated $\sqrt{\mu_{eff}}$ follows a linear relation with saturation magnetization
Magneto capacitance and Magnetoelectric coupling: Relative amount of phases

- Negative magnetocapacitance is due to magnetostriction
- The non-linear nature of magnetocapacitance is the compound effect of magnetostriction and number density of BT-NF interface

- ME response depends on piezoelectricity
- Lower the concentration of ferroelectric phase the lower the coupling coefficient
- The increased mole% in NF introduces mismatches in BT/NF interface as the coverage of NF grain by BT decreases
EFFECT OF POWDER PROCESSING
Microstructure: connectivity of the constituent phases

Not much difference in BT grain size range as well as NF grain size produced by three different route

NF cluster formation decreases

AC BT-NF: 70-30 > SS BT-NF:70-30 > HP BT-NF: 70-30

Microstructure may affect functional properties of composite
Effect of powder processing on relative permittivity

- Dielectric dispersion at low frequency
- Difference in Relative permittivity \(\Rightarrow\) Connectivity of the ferrite phases
- Dielectric polarization follows the order:
  
  Autocombustion \(<\) Solid-state \(<\) Hybrid precipitation

- Fine grained NF embedded in BT matrix provides more BT-NF interface – hence high \(\varepsilon_r\)
Comparative Impedance at higher temperature—the effect of processing

250 °C

Impedance $\rightarrow$ correlated to microstructural features and hence the connectivity of the constituent phases of ferrite

More number of grain-grain boundary in between the electrodes are present in samples obtained by hybrid precipitation

<table>
<thead>
<tr>
<th></th>
<th>Solid state BT-NF:70-30</th>
<th>Autocombustion BT-NF:70-30</th>
<th>Hybrid precipitation BT-NF:70-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_g$ (kΩ·cm$^{-1}$)</td>
<td>32.7</td>
<td>32.9</td>
<td>180.3</td>
</tr>
<tr>
<td>$R_{gb}$ (kΩ·cm$^{-1}$)</td>
<td>1212.5</td>
<td>1024.2</td>
<td>1119.4</td>
</tr>
</tbody>
</table>
Effect of powder processing on Magnetocapacitance and Magnetoelectric coupling

- $\alpha_{ME}$ increases up to a certain Field-after reaching a maxima it decreases
- ME coupling depends on the powder synthesis technique

Microstructure does not have significant role to alter the Magnetocapacitance
# Processing effect on Magnetoelectric coupling

<table>
<thead>
<tr>
<th>Processing route (BT-NF: 70-30)</th>
<th>Highest $\alpha_{ME}$ obtained (mV.cm(^{-1}).Oe(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid-state</td>
<td>1.2</td>
</tr>
<tr>
<td>Autocombustion</td>
<td>1.11</td>
</tr>
<tr>
<td>Hybrid precipitation</td>
<td>1.21</td>
</tr>
</tbody>
</table>

- Processing route: BT-NF: 70-30
- Highest $\alpha_{ME}$ obtained: mV.cm\(^{-1}\).Oe\(^{-1}\)
CONCLUSIONS

- BT-NF composite are thermo-chemically stable up to the sintering temperature (1200 °C).

- Processing has strong influence on the distribution hence connectivity of constituent phases.

- Dielectric behaviour depends on the constituent phase amount as well as powder synthesis technique.

- Conduction process in this composite is governed by ‘small polaron hopping’.

- The composites show ferromagnetic and lossy ferroelectric behaviour.

- Magnetostriction and magnetoresistance have influence on magneto-dielectric effect.

- Magnetostriction and the distribution of ferrite phase affect ME behaviour of the composites.
Thank You