INTRODUCTION

From the literature, it is observed that there is a renewed interest in investigations of magnetoelectric systems during the post 1993 period. The bilayers, multilayers and composites of piezomagnetic and piezoelectric systems have shown a substantially large magnitude of magnetoelectric coefficients. The magneto-electric composites are mechanically sturdy and could be a good candidate to form various devices based on ME phenomena as conceptualized in a review by Wood and Austin.

BaTiO$_3$ (BT) is known to be ferroelectric material possessing useful values of electromechanical coupling. Additionally being a lead free piezoelectric material, the BT has been looked upon as an environmental friendly alternative to the PZT. Further the Co$_{1-x}$Mg$_x$Fe$_2$O$_4$ (MCFO) is observed to be a magnetostrictive phase possessing high values of resistivity $\rho$, saturation magnetization $M_s$, coefficient of magnetostriction $\lambda$ and moderate value of the coercive field $H_c$. Therefore BT and MCFO are selected to form the magnetoelectric composites and the investigations are carried out on these systems.

The present paper reports the structural and morphological investigations on the MBT composites. Further owing to the virtues of complex impedance spectroscopy, the dielectric and the complex impedance properties of the composites are determined and analyzed to understand different relaxation processes occurring in these systems. The paper also presents the variations of
dynamic magnetoelectric coefficient as a function of the compositional variation and sintering temperature.

**MATERIAL AND METHODS**

**Synthesis of MCFO**

High purity (>99.0%) Magnesium Nitrate Mg(NO$_3$)$_2$·6H$_2$O, Cobalt Acetate Co(CH$_3$COO)$_2$·4H$_2$O and Ferric Nitrate 2Fe(NO$_3$)$_3$·9H$_2$O of AR grade are used as precursors while KOH is used as a precipitating agent for hydroxide co-precipitation route. The Mg(OH)$_2$ is partially soluble in water but insoluble in alkaline medium and therefore the precipitates are washed in dilute alkaline medium, using NH$_4$OH, maintaining pH between 9 to 10. The filtered precipitate is exposed to infrared radiation (IR) for evaporation of the traces of H$_2$O. The dry precipitate thus formed is used for further investigations and heat treatment for the formation of MCFO. The precipitate is pre-sintered at 1100°C while the final sintering has been carried out at 1200°C for 12 hours.

Initially Co$_{1-x}$MgxFe$_2$O$_4$ has been synthesized for varying x between 0.1 and 0.5, to determine a composition possessing optimum parameters for the formation of a magnetostrictive phase in the ME composites. It has been observed that x = 0.3 composition has high values of $\rho$, $M_s$, $\chi$ and low value of H$_c$ and therefore the composition x = 0.3 is a favorable composition for its selection and further investigations on the ME composites.

**Synthesis of BT**

The nano powder of BT has been synthesized using a similar process but employing Barium Nitrate Ba(NO$_3$)$_2$ and Potassium Titanium Oxalate K$_2$TiO(C$_2$O$_4$)$_2$·2H$_2$O as precursors. The KOH has been employed as a precipitating agent. For complete precipitation of Ba(OH)$_2$ and TiO(OH)$_2$, the molar ratio of KOH to (BaTi) of 1.6 has been used, based on the earlier reports. To synthesize BT in tetragonal phase the sintering temperature is required to be more than 1250°C therefore the precipitates are pre-sintered at 1200°C for 16 hours while the final sintering is carried out at 1280°C for 16 hours.

**Formation of Composites**

The nano powders of MCFO and BT thus synthesized are used to form the ME composites using following formula.

\[ X \text{MCFO} + (1-X) \text{BT} + 2 \text{wt} \% \text{Bi}_2\text{O}_3 \]

for $X = 0.2$, 0.3, 0.4, 0.5 and 0.6.

The composites are here further termed as 0.X MBT. The level of MCFO i.e. value of X is selected, so as to achieve the composites with sufficient resistivity. The high value of $\rho$ permits the poling of the samples for electric field $E > 3.5$ KV/cm. The restriction of $x=0.6$ is arrived at by performing initial work on these composites and subsequent measurements of the resistivity. Further $\text{Bi}_2\text{O}_3$ is used as a sintering aid to lower the temperature of sintering and achieve higher levels of densification. The composites are pressed in the form of pellets of diameter 1cm and thickness 1.5mm for further process of investigations. To understand the effect of sintering temperature on the physical properties of ME composites the composites are sintered at three different sintering temperatures viz. $T_s = 1075°C$, 1150°C and 1225°C for 8 hours each.

Here HP4284A LCR-Q meter is used for the purpose of the measurement of dielectric constant and complex impedance while a custom built setup is used for the measurement of magnetoelectric properties.

**RESULTS AND DISCUSSION**

**XRD Studies and particle size**

The individual powders of MCFO and BT are subjected to the X-ray analysis after the pre-sintering and final sintering processes. The XRD spectra of MCFO are observed to be in accordance with the JCPDS data for the parent compositions of Co and Mg ferrites. Essentially XRD analysis shows that the MCFO is formed in cubic spinal crystal structure with a = 8.3685 Å. It is also observed that no additional peak corresponding to any impurity phase is present in the XRD spectrum. The particle size analysis of MCFO is performed using Debye Scherrer's equation and is observed to be ~ 44 nm.

The XRD spectrum of BT is observed to be in accordance with the JCPDS data and earlier
Here the particle size is estimated using Williamson Hall method and is observed to be nearly 132 nm. Therefore it appears that the hydroxide co-precipitation route could be used to synthesize nano crystalline BaTiO$_3$ possessing the tetragonal phase required to form a piezoelectric ceramic.

Fig.1 and 2 show the XRD spectra of 0.2MBT and 0.5MBT composites sintered at $T_s = 1225 ^\circ$C. It has been observed that the reflections corresponding to the BT phase and MCFO phase could be distinctly identified. The XRD spectra for all other compositions of MBT composites i.e. $X = 0.2$ to $X = 0.5$ and for all other sintering temperatures i.e. $T_s = 1075 ^\circ$C, 1150$ ^\circ$C and 1225$ ^\circ$C are similar in nature with the spectra in fig. 1 and 2. Here no reflections corresponding to any impurity phase is observed and composites are exclusively bi-phase systems.

The table 1 shows the variation of the ratio of intensities of (311) plane of MCFO and (101) plane of BT. From the table it is observed that the relative intensity of the (311) reflection of the ferrite phase increases monotonically with increase in $X$, this confirms the formation of the true bi-phase composites.

**Microstructural Analysis**

MBT composites are subjected to the micro-structural analysis using scanning electron micrographs. Fig. 3 and 4 shows the SEM photographs of the MBT composites sintered at 1150$ ^\circ$C for $X = 0.3$ and $X = 0.6$. It could be seen from the fig. that the sintering at 1150$ ^\circ$C has caused formation of grain compacts. It could also be seen that though the individual particles are of sub-micron size the grain compact possess average diameter in the micron range. Here the average diameter of the grain compact is observed to increase as the $X$ increases from 0.2 to 0.6. Therefore the effect of ferrite phase is towards acceleration in the formation of the grain compacts. This could be due to the fact that the ferrites are softer for sintering as compared to hard sintering phase like BaTiO$_3$.

The effect of sintering temperature on the microstructure of MBT composite is also analyzed. The fig.5, 6 and 7 shows the SEM pictures for $X = 0.3$ sintered at $T_s = 1075 ^\circ$C, 1150$ ^\circ$C and 1225$ ^\circ$C respectively. From these figures it could be seen that as the sintering temperature increases from 1075$ ^\circ$C to 1225$ ^\circ$C the average grain diameter increases which is in confirmation with earlier report$^1$. Because of the densification voids become apparent in the microstructure.

**Dielectric properties**

Fig.8 shows variation of dielectric constant $\varepsilon_r$ as a function of temperature for MBT composites sintered at $T_s = 1225 ^\circ$C. Similar behavior is observed for the MBT composites sintered at $T_s = 1075 ^\circ$C and 1150$ ^\circ$C. The variation of $\varepsilon_r$ (dielectric constant) with $T$ is observed to pass through a diffused phase transition at $T = 126 ^\circ$C which is the Curie temperature of BT. The earlier report indicate that $\varepsilon_r$ in these systems possess two contributions one due to the ferroelectric nature of BT and other due to the interfacial polarization occurring at the boundaries between BaTiO$_3$ and MCFO phases$^{12}$. Here the diffused nature of the phase transition could be attributed to the contribution of interfacial polarization in these systems.

To understand this feature further the frequency variation of the dielectric constant on the MBT composites is also studied. Fig.9. Shows the variation of $\varepsilon_r$ with $T$ of MBT composite for $X = 0.2$ at $T_s = 1075 ^\circ$C and for frequencies varying between 100 Hz and 1 MHz. It is observed that the transition temperature does not change with the varying frequency and shows that no relaxor type contribution could be expected in this composition$^{13}$. The increase in $\varepsilon_r$ in the paraelectric region is prominent for lower frequencies. This feature is attributed to the presence of interfacial polarization at BT and ferrite phases, due to the difference in the resistivities of these phases. The observations of $\varepsilon_r$ with $f$ are similar for all other compositions of MBT and for all other sintering temperatures.

**Complex impedance spectroscopy**

The complex impedance spectra of these composites are also investigated for these systems to understand the relaxation processes occurring in the ferroelectric phase and at the interfaces between ferrite and ferroelectric phases.

Fig. 10, 11 and 12 shows the variation of $\text{IZ}^\prime$ with $Z'$ of MBT composites for $X = 0.2$, 0.4 and
Fig. 1: XRD SPECTRA OF 0.2MBT Sintered at $T_s = 1225^\circ C$

Fig. 2: XRD SPECTRA OF 0.5MBT Sintered at $T_s = 1225^\circ C$

Fig. 3: SEM picture of MBT for $X=0.3$ for $T_s = 1150^\circ C$
Fig. 4: SEM picture of MBT for $X=0.6$ for $T_s = 1150^\circ C$

Fig. 5: SEM picture of MBT for $X=0.3$ for $T_s = 1075^\circ C$.

Fig. 6: SEM picture of MBT for $X=0.3$ for $T_s = 1150^\circ C$. 
Fig. 7: SEM picture of MBT for X=0.3 for T_s = 1225°C

Fig. 8: Variation of Dielectric constant (εr) with Temperature of MBT Composites for T_s = 1225°C at 1 KHz

Fig. 9: Variation of Dielectric constant (εr) with Temperature of 0.2MBT Composite sintered at 1075°C for varying frequency
Fig. 10: Variation of $Z''$ as $Z'$ of MBT Composite for $x = 0.2$ and $T_s = 1075^\circ C$

Fig. 11: Variation of $Z''$ as $Z'$ of MBT Composite for $x = 0.4$ and $T_s = 1075^\circ C$

Fig. 12: Variation of $Z''$ as $Z'$ of MBT Composite for $x = 0.6$ and $T_s = 1075^\circ C$
**Fig. 13**: Variation of $\epsilon'$ as log $\omega$ of MBT Composites at $T_s = 1150^\circ$C

**Fig. 14**: Variation of $\epsilon''$ as log $\omega$ of MBT Composites at $T_s = 1225^\circ$C

**Fig. 15**: Variation of ME coefficient ($\alpha$) with $x$ for MBT series
0.6 respectively at \( T_s = 1075^\circ\text{C} \) in the frequency range 20 Hz to 1 MHz. Here \( Z' \) and \( Z'' \) represent real and imaginary parts of the complex impedance. Two separate contributions one due to interfacial polarization and other due to the bulk of ferroelectric grain are apparent from the observed complex impedance spectra. The contribution due to interfacial polarization is predominant in low frequency region while the contribution due to the bulk capacitance of BT occurs at higher frequencies. Employing the curve fitting techniques, these two contributions are separated out and the values of corresponding resistances and capacitances are determined. The bulk capacitance \( C_1 \) of the material is represented by high frequency semicircle which is due to ferroelectric phase. Table 2, 3 and 4 show the magnitudes of \( R_1 \), \( C_1 \) and \( F_1 \) of MBT composites sintered at 1075°C, 1150°C and 1225°C respectively. Here \( R_1 \), \( C_1 \) and \( F_1 \) correspond to bulk resistance, bulk capacitance and resonant frequency of high frequency semicircle respectively.

From the table it could be seen that as \( X \) increases the value of \( C_1 \) representing bulk capacitance decreases. This feature is attributed to the reducing content of ferroelectric phase as \( X \) increases.

### Table 1: Variation of ratio of relative intensity I of 311 planes of MCFO and BT sintered at 1150°C and 1225°C

| Composition (x) | \( \frac{I}{I_0} \) ratio | \( \frac{I}{I_0} \) ratio |
|----------------|--------------------------|--------------------------|
| 0.2            | 24.6                     | 23.5                     |
| 0.3            | 37.0                     | 30.0                     |
| 0.4            | 61.7                     | 45.6                     |
| 0.5            | 64.5                     | 53.15                    |
| 0.6            | 87.0                     | 77.5                     |

### Table 2: Magnitudes of \( R_1 \), \( C_1 \) and \( F_1 \) of MBT series sintered at 1075°C

| X     | \( R_1 \) (ohm) | \( C_1 \) (pf) | \( F \) (Hz) |
|-------|----------------|---------------|-------------|
| 0.2   | 26300000       | 1195.62       | 50          |
| 0.3   | 58300000       | 990           | 120         |
| 0.4   | 99300000       | 201.2         | 80          |
| 0.5   | 13460000       | 122.95        | 100         |
| 0.6   | 36340000       | 226           | 20          |

### Table 3: Magnitudes of \( R_1 \), \( C_1 \) and \( F_1 \) of MBT series sintered at 1150°C

| X     | \( R_1 \) (ohm) | \( C_1 \) (pf) | \( F \) (Hz) |
|-------|----------------|---------------|-------------|
| 0.2   | 14380000       | 186.75        | 60          |
| 0.3   | 18360000       | 146           | 60          |
| 0.4   | 30910000       | 105.5         | 50          |

### Table 4: Magnitudes of \( R_1 \), \( C_1 \) and \( F_1 \) of MBT series sintered at 1225°C

| X     | \( R_1 \) (ohm) | \( C_1 \) (pf) | \( F \) (Hz) |
|-------|----------------|---------------|-------------|
| 0.2   | 12070000       | 439.618       | 30          |
| 0.3   | 16310000       | 427.53        | 25          |
| 0.4   | 41670000       | 126.58        | 30          |
| 0.5   | 28140000       | 188.6         | 50          |
| 0.6   | 15140000       | 176.9         | 60          |

### Table 5: Variation of \( a \) for MBT series

| S. No. | X     | a S. T. 1075°C mV Oe\(^{-1}\) cm\(^{-1}\) | a S. T. 1150°C mV Oe\(^{-1}\) cm\(^{-1}\) | a S. T. 1225°C mV Oe\(^{-1}\) cm\(^{-1}\) |
|--------|-------|------------------------------------------|------------------------------------------|------------------------------------------|
| 1.     | 0.2   | 0.2585                                   | 0.776                                    | 0.351                                    |
| 2.     | 0.3   | 0.2559                                   | 0.126                                    | 0.261                                    |
| 3.     | 0.4   | 0.347                                    | 0.321                                    | 0.306                                    |
| 4.     | 0.5   | 0.37                                     | 0.257                                    | 0.183                                    |
| 5.     | 0.6   | 0.3053                                   | 0.242                                    | 0.543                                    |

Dielectric spectroscopy

The complex impedance spectra has been used to determine the complex dielectric constant \( \epsilon' \) and \( \epsilon'' \) using the equations

\[
\epsilon' = \frac{Z'}{[\omega C_0 ((Z')^2 + (Z'')^2)]}
\]

and

\[
\epsilon'' = \frac{Z''}{[\omega C_0 ((Z')^2 + (Z'')^2)]}
\]
Fig. 13 and 14 shows the variation of $\varepsilon'$ and $\varepsilon''$ as a function of the frequency for varying $x$ for the MBT composites sintered at 1150°C and 1225°C respectively. It is observed that the $\varepsilon'$ decreases very fast at lower frequencies less than 1 KHz which represents the presence of interfacial polarization in these compositions. For frequencies above 500 KHz a small region of sharp decrease is recorded which occurs due to additional relaxation process predominant at very high frequencies. The $\varepsilon'$ is also observed to decrease with increase in frequency. This indicates predominant contribution of the conductivity term in $\varepsilon'$.

**Magnetolectric measurements**

The magneto-electric measurements are carried out with the help of a experimental setup designed in our Laboratory.

The dynamic magnetolectric coefficient $\alpha$ has been measured at 850 Hz for variation of $x$ and $T_s$. The table 5 shows the variation of $\alpha$ for different values of $x$ for MBT composites and for different sintering temperatures while fig. 15 shows variation of $\alpha$ as a function of $x$ for MBT series. The $\alpha$ is observed to pass through a maximum for $x = 0.4$. Also the $\alpha$ is observed to decrease with increasing $T_s$.

Here from the analysis of SEM it has been observed that as the sintering temperature increases the average grain diameter of the composite increases. The increase in grain diameter causes increase in voids around individual grains. This may cause effective reduction in the electromechanical coupling coefficient of the samples and therefore the $\alpha$ decreases with increase in $T_s$.

Essentially it is observed that hydroxide co-precipitation route could be used successfully for the synthesis of nano-crystalline MCFO and BT powders. The MBT composites show a significant contribution of interfacial polarization due to difference in the resistivities of ferrite and ferroelectric phases. The dynamic magnetolectric coefficient $\alpha$ is observed to pass through a maximum for $x = 0.4$ and the magnitude of $\alpha$ decreases with increase in $T_s$ due to the reduced magnetolectric coupling for sintering at higher temperatures.

**REFERENCES**

1. Jungho Ryu, Alfread canazo, Kenji uchino & Hyoun-El KIM, Journal of Electroceramics 7: 17-24 (2001).
2. G.Shrinivasan, E.T.Rasmussen, J. Gallegal and R.Shrinivasan, Physical Review B, 64: 214408 (2001).
3. G.Shrinivasan, F2.T Rasmussen, B.J.Levin & R. Hayes Physical Review B 65: 134402 (2001).
4. V.M.Petrov, M.I.Bichurin, G.Srinivasan MEIPIC-5-Sudak (Ukraine) (2003).
5. E.Wood and A.E.Austin, Int. J. Magnet 5:303 (1974).
6. Gang Xu, Wenjian Weng, Jianxi Yao, Piyi Du, Gaorong Han, "Microelectronics Engineering" 66: 568-573 (2003).
7. S.K.Lee, T.J.Park, G.J.Choi, K.K.Koo, Sang Woo Kim, Materials Chemistry and Physics 82: 742-749 (2003).
8. Amitava Chakraborty and Himadri SMaiti, Ceramic International, 25: 115 (1999)
9. S.S.Veer,D.J.Salunkhe, S.V.Kulkarni, S.B.Kulkarni, P.B.Joshi Indian Journal of Engg. & Materials Sciences. 15 121(2008)
10. Y.K.Fetisov, A.A.Bush, K.E.Kameutsev, G.Srinivasan, Solid State Communication 132: 314-324.(2004).
11. D.J.Salunkhe,S.S.Veer, S.V.Kulkarni, S.V.Kulkarni, P.B.Joshi Journal of Instrumentation Society of India 4: 294 (2008).
12. C.G.Koops Phys.Rev.6, 108 (1997).
13. S.L.Kadam, K.K.Patankar, V.L.Mathe, B.K.Chaugule J. Electroceramics 9: 193 (2002).
14. R.N.P.Choudhary and Awalendra K.Thakur, NSFD-XIII, Ferroelectrics and Dielectrics, 287-293 (2004).