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“Study on the iron-deficient non-stoichiometry driven electromagnetic and magnetoelectric properties of multiferroic composites”

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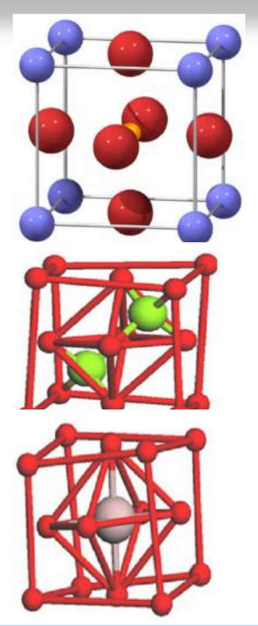
Introduction

- ❑ A **multiferroic composite material** is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produced a material with characteristics different from the individual components.
- ❑ **The multiferroic materials exhibit at least two ferroic orders (ferroelectric and ferromagnetic) simultaneously at room temperature.**
- ❑ Coupling between different order parameters can produce additional functionalities, such as a magnetoelectric (ME) effect.
- ❑ Magnetoelectric (ME) effect may be absent in the individual phases but is observed in the composites.

Crystal Structure



- ❑ Ferroelectric materials are belongs to the structure of perovskite type.
- ❑ General chemical formula of perovskite structure is **ABO_3**, where A is a mono- or di- or trivalent metal and B is a tri-or tetra- or pentavalent metal (example, BaTiO3, BiFeO3 , KNbO3 etc).
- ❑ Ferrite is the double oxide of iron and another metal. General chemical composition AB_2O_4

Objectives

(i) To synthesize (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] + (*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] (*x* = 0.00-0.12; *y* = 0.2, 0.5) composites by conventional solid state reaction method sintered at 1200ºC for 5h.

(ii)To study the phase formation of synthesized composites by X-ray diffraction technique.

(iii)To study the micro structural aspects of synthesized composites through SEM analysis.

(iv)To study the electric properties i.e. dielectric properties and ac conductivity.

(v) To study the magnetic properties i.e. magnetic permeability and magnetic loss

(vi) To study Magnetoelectric coupling coefficient.

Applications

- ❑ Transformers:
- ❑ Microelectronics:
- ❑ Memory devices
- ❑ Magnetic field Sensors
- ❑ Spintronics
- ❑ Transducers
- ❑ Filters
- ❑ Tunable devices

Sample Preparation

The set of magnetoelectric composites described by the general composition (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] + (*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] (*x* = 0.00-0.12; *y* = 0.2, 0.5). The composite under investigation were synthesized via the conventional solid-state reaction route.

In first step, the [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] ferroelectric phase was prepared using the raw materials of BaCO3, CaCO3, TiO2 and ZrO2.

The weighed powders in appropriate stoichiometry were mixed and ground thoroughly in an agate mortar using acetone as a medium for 6h was placed in alumina for calcining at 950 °C for 5h. The heating and cooling rates were set at 10ºC/min and 5ºC/min, respectively.

Afterward, the calcined power was reground again for 4h to make homogeneous powder.

In second step, the ferromagnetic phase [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] were prepared using NiO, CuO, ZnO and Fe2O3 as the starting materials and the synthesis process was same as the ferroelectric phase had already been explained.

The composites were synthesized by the above ferroelectric and ferromagnetic calcined powders according to the general composition mixed with polyvinyl alcohol (PVA) by using a hydraulic press in a die with pressure of 6400 psi to obtain the magnetoelectric composites.

Finally, the green pellets and toroid of the composites were sintered in air at 1200ºC for 5h.

Results and Discussion

X-Ray Diffraction (XRD) and FTIR Spectra

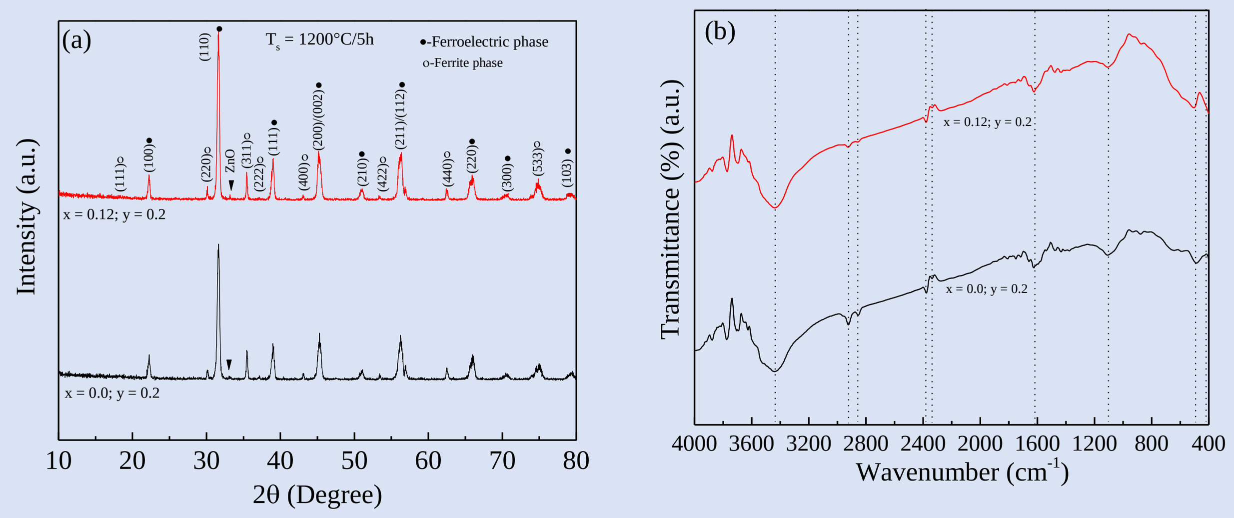


Fig. 1. (a) XRD patterns and (b) FTIR spectra of (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] + (*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] (*x* = 0.00, 0.12; *y* = 0.2) composites sintered at1200ºC for 5 h.

- ❑ The phase formation and the crystal structure of the individual phases and simultaneousness of the individual phases in the composites were confirmed by powder X-ray diffraction (XRD) and Fourier transform infrared spectroscopic (FTIR) analyses without any traceable secondary phase formation.
- ❑ Ferroelectric Peak positions reveals the perovskite structure.
- ❑ Ferromagnetic peak confirms the formation of cubic spinel structure.
- ❑ Lattice parameters of ferroelectric are obtained by, $\frac{1}{d_{hkl}^2} = \left(\frac{h^2+k^2}{a^2}\right) + \frac{l^2}{c^2}$
- ❑ Lattice parameters of Ferromagnetic is determined by the formula : $a_{Cubic} = d_{hkl}\sqrt{h^2+k^2+l^2}$

SEM Micrograph

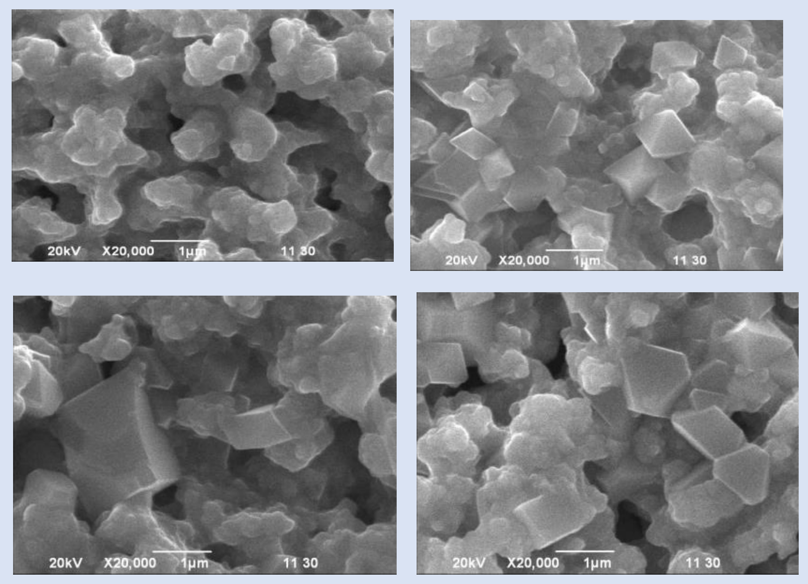


Fig. 2. SEM micrographs of (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] + (*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] (*x* = 0.00-0.12; *y* = 0.2) composites

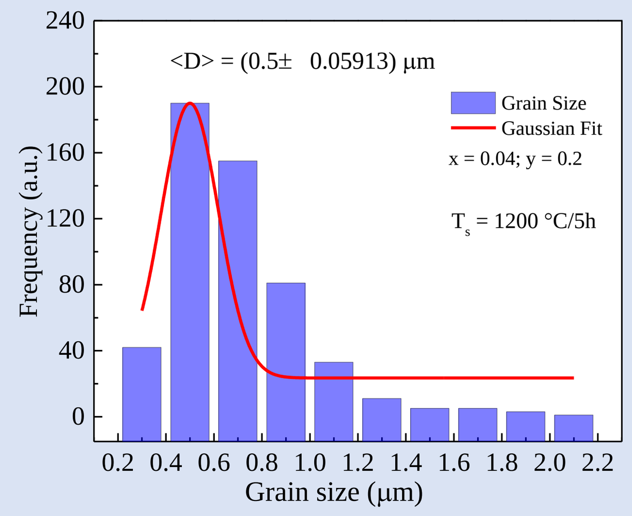


Fig. 3. Histogram of (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] +(*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] (*x* = 0.04; *y* = 0.2) composites

- ❑ The scanning electron microscopic (SEM) study ascertained the formation of grains that possessed polyhedral or irregular shapes and sizes with little agglomeration and porosity with iron-deficient non-stoichiometry .

Electrical properties

Dielectric Constant and Dielectric loss

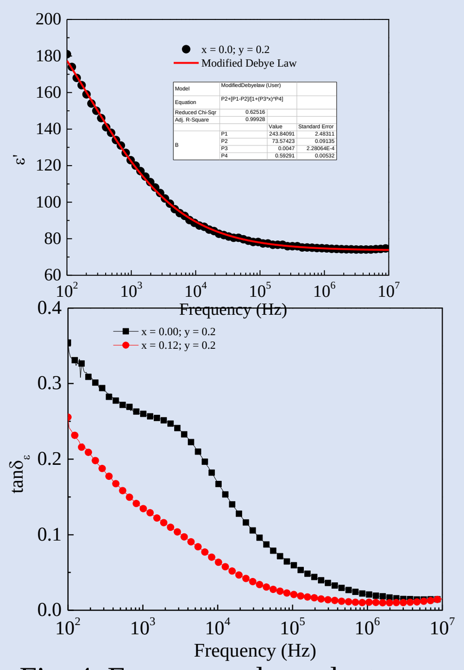


Fig. 4. Frequency-dependent dielectric constant (ε'): (a) *x* = 0.00; *y* = 0.2 (Modified Debye law) and dielectric loss ($tan\delta_E$).

- ❑ Real part of dielectric constant decreases with the increase of frequency.
- ❑ The dielectric dispersion at lower frequencies is due to the presence of the different types of polarizations such as dipolar, electronic, ionic and interfacial polarization.
- ❑ At higher frequencies, some of these polarizations do not follow the applied electric field and thus less contribution to dielectric constant and then it decreases.
- ❑ The electrical conductivity in composites material is due to hopping of electrons between the same element present in more than one valence state.
- ❑ Values of dielectric loss factor (tanδ) decrease very fast in the low frequency region and achieve almost constant value at high frequency region.
- ❑ The values are very high at lower frequencies due to high resistivity of grain boundaries and high electron hopping energies.
- ❑ The dielectric loss peak appears when the applied frequency is matched with hopping frequency, which arises according to Debye relaxation theory.
- ❑ **The dielectric loss arises mainly due to impurities and imperfections in the crystal lattice.**

AC conductivity

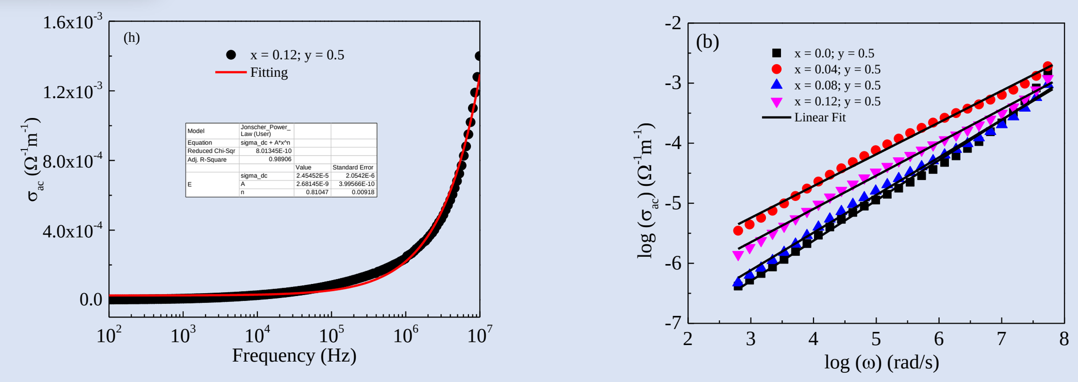


Fig. 5 (a) A typical fitted curve (red line) of σ_{ac} according to Jonscher’s power law (b) Variation of $log(\omega)$ vs. $log(\sigma_{ac})$ fitting data of (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] + (*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] (*x* = 0.00-0.12; *y* = 0.5) composites sintered at1200ºC for 5 h.

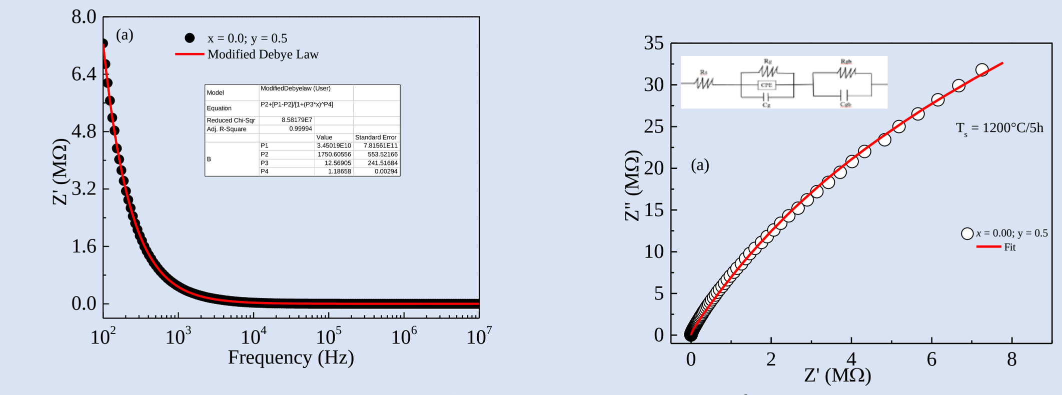


Fig. 6. Frequency-dependent (a) real part of complex impedance (Z') and (b) Fitted Nyquist plot of impedance curve with the equivalent circuit used to fit (inset) of (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] + (*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] (*x* = 0.00; *y* = 0.5) composites sintered at1200ºC for 5h.

Magnetic properties

Permeability

Magnetic loss

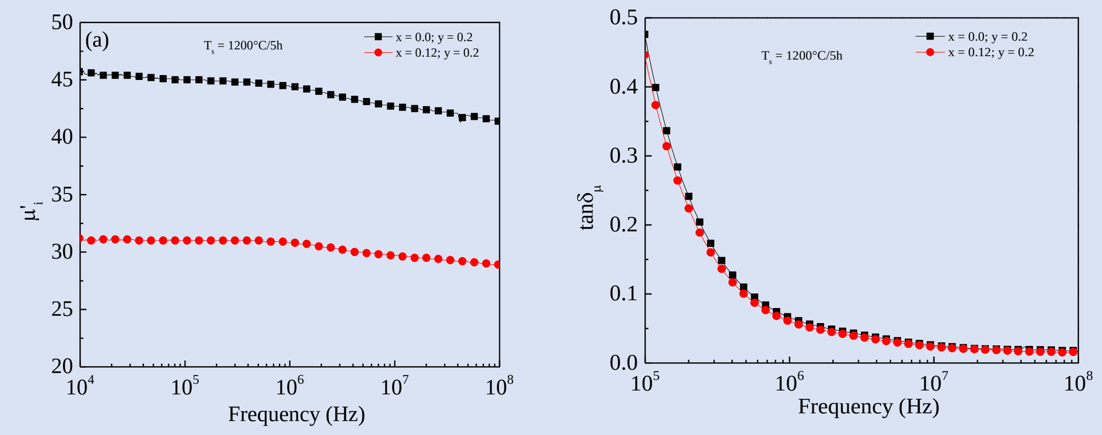


Fig. 7. (a) Frequency-dependent real part of permeability (μ_i') and (b) magnetic loss ($tan\delta_\mu$) of (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] + (*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] (*x* = 0.00, 0.12; *y* = 0.2) composites sintered at1200ºC for 5 h.

Magnetoelectric coupling coefficient

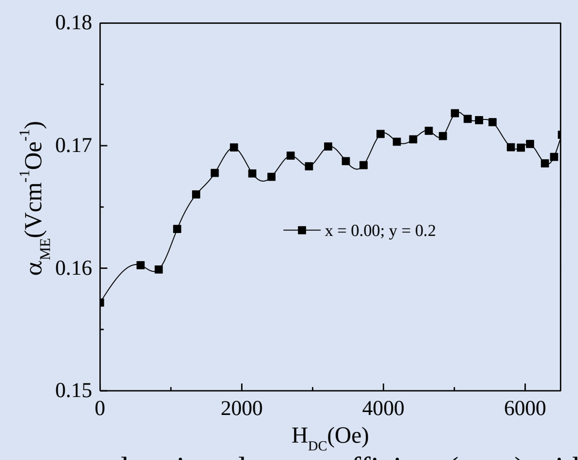


Fig. 8. Variation of magnetoelectric voltage coefficient (α_{ME}) with applied DC magnetic field of (1-*y*) [$Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$] + (*y*) [$Ni_{0.25}Cu_{0.13}Zn_{0.62}Fe_{2-x}O_{4-3x/2}$] composites: *x* = 0.0; *y* = 0.2.

Conclusions

- ❑ Multiferroic composites have been prepared by standard solid state reaction technique.
- ❑ XRD pattern reveals the coexistence of both the perovskite and ferrite phase in the composite.
- ❑ The average grain size of composites is found to be enhanced with the iron-deficient non-stoichiometry.
- ❑ Dielectric constant and frequency-dependent real part of complex impedance were fitted by Modified Debye law.
- ❑ Ac conductivity fitted according to Jonscher’s power law.
- ❑ Fitted Nyquist plot of impedance curve with the equivalent circuit used to fit all composites.
- ❑ The real part of initial permeability of composites decreases with the iron-deficient non-stoichiometry
- ❑ The magnetoelectric voltage coefficient was measured for all composites and highest value was found (~ 0.17 V/cm-Oe).

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