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# Synthesis and electrical properties of Lead-free Magneto Electric (ME) composites

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**Abstract:** Polycrystalline composites of Barium cobalt titanate (1-x) $(Ba_{0.8}Co_{0.2})$ $TiO_3$ [BCT] and Cobalt zinc ferrite x $(Co_{0.6}Zn_{0.4})$ $Fe_2O_4$ [CZF] (x=0.00, 0.4, 0.3, 0.2, 0.1, 1.0) were prepared by a modified wet chemical method followed by a high temperature sintering process. X-ray diffraction (XRD) studies at room temperature confirmed the formation of perovskites - spinel structure and on the basis of XRD pattern, the dominant peak has been observed at 2 =$32^0$ and $24^0$ and Miller indices (100) and(110) planes, respectively. Dielectric studies of composites prove that the effect of ferrite in the composites is to shift the ferroelectric phase transition to the higher temperature side with a broadened Curie temperature transition. The conduction at low temperature is due to impurities, whereas at higher temperature it is due to polaraon hopping.

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## Introduction:

Composite materials containing both ferroelectric and ferromagnetic phases have recently attracted a great deal of attention because of their potential applications in practical electronic devices, greater design flexibility and large magneto electric response. They can also be operated at room temperature. So they can be used as multifunctional devices such as magnetic-electric transducers and sensor applications. When ferromagnetism and ferroelectric property coexist in a material, magnetic-electric effect based phenomena are expected due to the interaction between the magnetization and the electric polarization. There are very few single-phase materials with such combined properties. Ferrites and ferroelectric materials are used in a large family of microwave and millimeter-wave devices. Spinel ferrites have been widely studied due to their interesting properties like high resistivity, mechanical hardness, remarkable stability and promising memory storage capacity. They have a wide range of applications in microwave absorbance, number of electronic devices as, radio, TV sets, high frequency transformers, memory core devices, rod antennas, and read-write heads for highspeed digital tape or disk recording. Current ferrite components, however, present two critical problems for advanced system applications: large size and high cost. Ferroelectric components, on the other hand, provide solutions both in size and cost. Size reduction arises from the large relative dielectric constants. These components are also tunable with the application of a modest voltage. It is likely that ferrite–ferroelectric composites could be used to produce small, low-cost, and highly tunable elements for microwave applications. Because of the wide variety of possible applications, there has been considerable interest in composite materials. Previous works on multifunctional ferrite–ferroelectric composite materials have emphasized static magnetization properties and complex permeability and permittivity. In this work $(Co_{0.6}Zn_{0.4})$ $Fe_2O_4$ was selected as a magnetic material because Cobalt-zinc ferrites [CZF] have high resistance, high Curie temperature and low dielectric permittivity and $(Ba_{0.8}Co_{0.2})$ TiO3 as a ferroelectric because Barium cobalt titanate [BCT] has high dielectric constant, high tunability, and low dielectric loss. The Curie temperature of Barium cobalt titanate [BCT] varies with the composition of Cobalt. The aim of the present paper is to study the dependence of dielectric constant (e) and dielectric loss (e") on the frequency and the temperature.

**Objectives**:

The objective is to measure dielectric properties of the sample with impedance analyzer instrument. The study of electrical conductivity is very important since the associated physical properties are dependent on order and nature of conductivity in these materials. In view of increased interest in [BCT] and [CZF] based solid solutions, the present work shows detailed studies of electrical behaviour in the temperature range from room temperature to 500°C. The AC impedance method is a promising non-destructive testing method for analyzing ferroelectrics. The electrical data are often presented in terms of permittivity (e). The frequency dependent properties of a dielectric can be described via the dielectric constant. They are related as

$$e^* = e - je''$$

The above expression offers wide scope for graphical analysis. The popular forms of data presentations is the plots of e, e" vs. frequency. The above dielectric parameters will normally result in peaks when plotted against frequency. The observed peak within the frequency range varies as temperature increases. e* formalism helps in determining conductivity for comparative purposes. The electrical formalism helps to understand the dielectric behaviour of the composites.

**Methodology:**

**Preparation of composites:** Wet chemical method was used for the composite preparation. Composite phase [BCT] powder was synthesized by using barium nitrate, cobalt nitrate, and titanium (IV) butaoxide as precursors for barium, cobalt, and titanium, respectively. Citric acid was used as solvent and 2-methoxy ethanol was used to stabilize titanium (IV) butaoxide. Stoichiometric proportions of barium nitrate and cobalt nitrate powder were dissolved in 10 and 5mL of distilled water, respectively, by continuous magnetic stirring at 60°C for half an hour. The two solutions were then mixed at 110°C for 2 h. 2-methoxy ethanol (2–4 mL) was added in titanium (IV) butaoxide (0.11 mol) to form a separate solution at room temperature. Ba–Co solution was added drop by drop, into Ti solution and the pH of the solution was maintained in the range of 2.5–4.0 by adding buffering agents. Distilled water was added to the gel and the solutions were mixed by stirring on a hot plate with a magnetic stirrer. After that it was kept in the oven and heated to 200° C for 2 h. This resulted in the formation of amorphous powder of [BCT]. The amorphous powder was then calcined at 650°C for 2 h in a muffle furnace. The calcined powder was ground in a mortar pestle to obtain fine powder. The [CZF] was prepared by citrate precursor method as reported. Then, both the calcined powders (1-x) $(Ba_{0.8}Co_{0.2})$ TiO3-x $(Co_{0.6}Zn_{0.4})$ $Fe2O_4$ with (x=0.00, 0.4, 0.3, 0.2, 0.1, 1.0) were mixed together. The powder composites were uniaxially pressed into cylindrical pellets of diameter 10mm and thickness 1mm using a hydraulic press at a pressure of 50 MPa and sintered at 850°C for 4 h.

**Structural Characterization:** Product densities were determined from weight and dimension measurements. The crystal structures and lattice parameter were examined by an X-ray diffraction (XRD) technique using a Philips Analytical, X'pert-MPD, employing Cu-K radiations under the conditions 50 kV and 40mA. The samples were scanned at an interval of 0.038/min for 2u in the range 10°–80°. The identification of the peaks was carried out using the Topas23 refinement program.

**Electrical characterization:** For dielectric measurements, the disk-shaped samples were ground on SiC paper to reduce the thickness to less than 1mm and coated with silver paste. Dielectric constant, loss tangent and impedance were determined by PSM1735 Impedance Analyzer at frequencies of 100Hz to 10 MHz; samples were heated from room temperature to 500$^0$C in a Carbolite (MTF9/15/130) tube furnace.

**Results and Discussion :**

**Structural analysis:** XRD pattern of composites reveals the mixed spinel-perovskite structure. The intensity of their diffraction peaks is dependent on the amount of the corresponding phase. Within the resolution limit of the XRD equipment no other phases were detected, confirming the successful preparation of two phase composite materials in this system, i.e., the ferroelectric [BCT] is compatible with ferrite [CZF]. The XRD graph pattern exhibits several peaks that can be observed at 2q =32$^0$ and 24$^0$. Based on the XRD graph patterns, it shows that the crystallization of (1-x) (BaCoTiO$_3$) - (x) (CoZnFe$_2$O$_4$) completely formed with composition of (x=0.00, 0.4, 0.3, 0.2, 0.1, 1.0). The crystallite size D, can be calculated based on the dominant peak at 2q =32$^0$using Scherer's equation as

D= kl / Bcosq

Where l is the X-ray wavelength (1.5406 x 10$^{-10}$m), k is the Scherer's constant (0.94), B is the broadening of the diffraction line measured at the half of its maximum intensity in radians and è is the angle of diffraction.

The XRD patterns of (1-x) (Ba$_{0.8}$Co$_{0.2}$) TiO3-x (Co$_{0.6}$Zn$_{0.4}$) Fe2O$_4$ [BCT-CZF] in the 2 è range of 10$^0$-90$^0$ are shown in the given figures.

Figure 1 shows the XRD patterns for the composites with x=0.

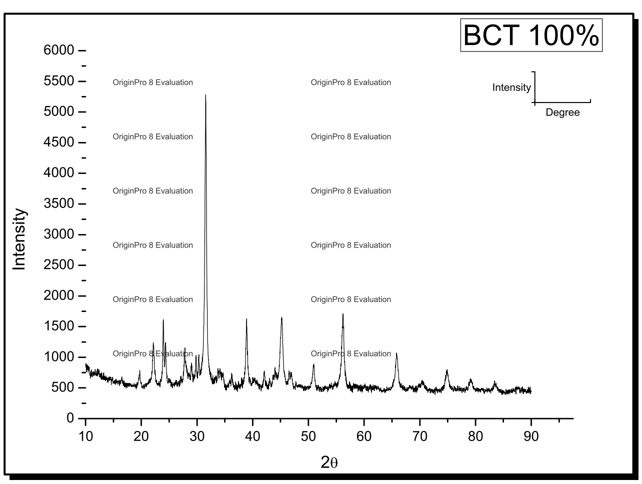


**Fig. 1. Room Temperature XRD pattern of (1-x) (Ba$_{0.}$8Co$_{0.2}$TiO$_3$)/x(Co$_{0.6}$Zn$_{0.4}$Fe $_2$O$_4$) ceramic at 600$^0$c**

Figure 2 shows the XRD pattern for the composites with x=0.1.

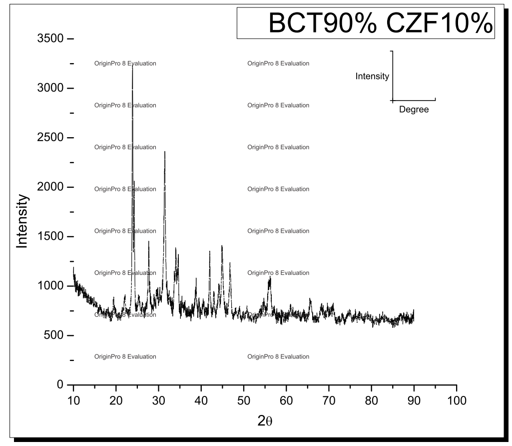


**Fig. 2. Room Temperature XRD pattern of (1-x) (Ba$_{0.}$8Co$_{0.2}$TiO$_3$)/x(Co$_{0.6}$Zn$_{0.4}$Fe $_2$O$_4$) ceramic at 600$^0$c**

Figure 3 shows the XRD pattern for the composites with x=0.2.

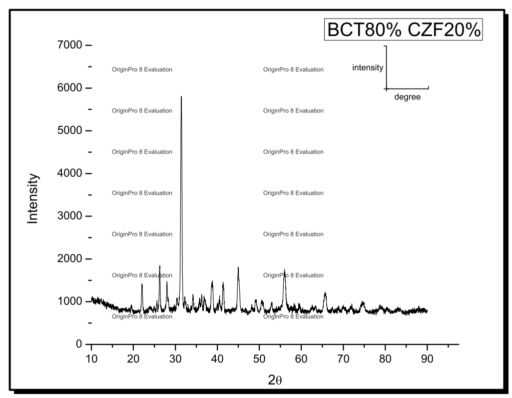


**Fig. 3. Room Temperature XRD pattern of (1-x) (Ba$_{0.}$8Co$_{0.2}$TiO$_3$)/x(Co$_{0.6}$Zn$_{0.4}$Fe $_2$O$_4$) ceramic at 600$^0$c**

Figure 4 shows the XRD pattern for the composites with x=0.3.

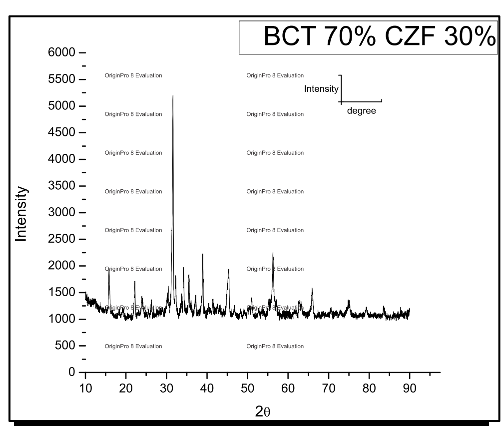


**Fig. 4. Room Temperature XRD pattern of (1-x) (Ba$_{0.}$8Co$_{0.2}$TiO$_3$)/x(Co$_{0.6}$Zn$_{0.4}$Fe $_2$O$_4$) ceramic at 600$^0$c**

Figure 5 shows the XRD pattern for the composites with x=0.4.

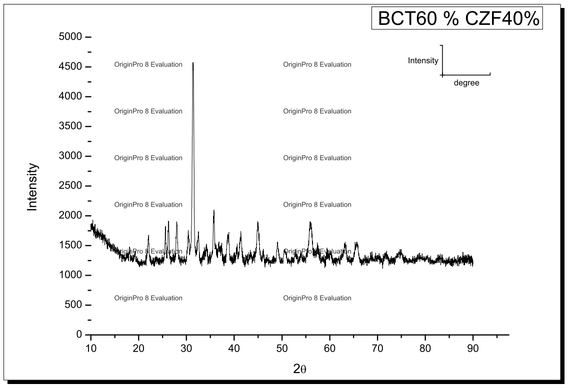


**Fig. 5. XRD pattern of (1-x) ($Ba_{0.8}Co_{0.2}$) $TiO_3$-x ($Co_{0.6}Zn_{0.4}$) $Fe_2O_4$ ceramic at room temperature with x=0.4.**

Figure 6: shows the XRD pattern for the composites with x=1.00.

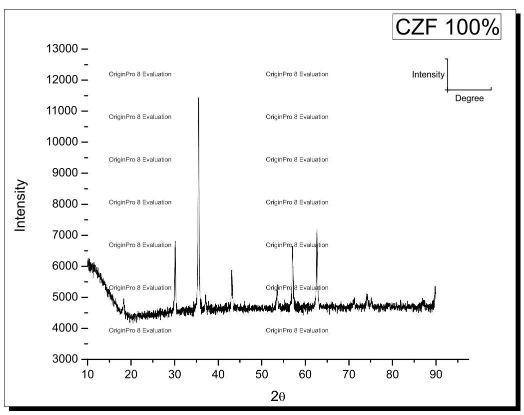


***Fig. 6. XRD pattern of (1-x) ($Ba_{0.8}Co_{0.2}$) $TiO_3$-x ($Co_{0.6}Zn_{0.4}$) $Fe_2O_4$ ceramic at room temperature with x=0.4.***

***Electrical characterization:*** The variation of dielectric constant (e) and dielectric loss (e'') of sintered sample of Barium cobalt titanate [BCT] and Cobalt zinc ferrite [CZF] with frequency and temperature i.e. e(w), e (T), e'' (w) and e'' (T) are shown in figure 7 to figure 10.

The dielectric properties of the samples were measured with impedance analyzer instrument. The dielectric measurement was analyzed within frequency range 100Hz to 10M Hz at room temperature. The dielectric permittivity value of the sample was calculated from the measurement of capacitance using equation

$$e_r = Cd/e_0A$$

## Conclusion :

Dielectric frequency curves shows that there is decrease of e with increase in frequency. The dielectric constant decreases with increase in frequency up to 10K Hz, beyond which it remains almost constant. At low frequencies electronic, ionic, dipolar and interfacial/ surface polarizations contribute to the dielectric constant. But for frequencies above 10k Hz the contribution from interfacial/surface polarization gets minimized. The decrease in e" i.e. dielectric loss for increase in frequency implies that up to a frequency of 10K Hz the ionic conduction and the electron capture process contributes to the polarization process.

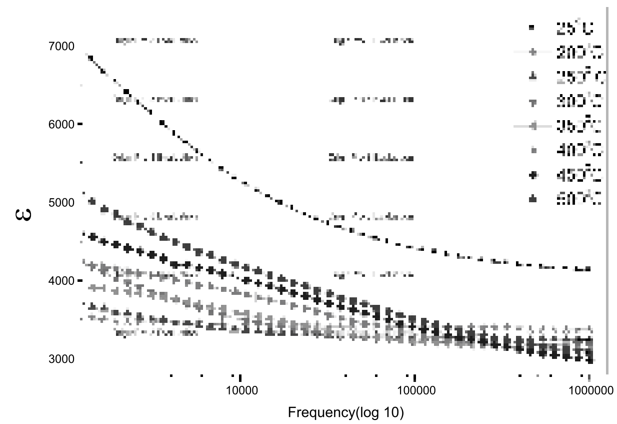


**Fig. 7. Variation of dielectric constant with frequency at different temperature.**

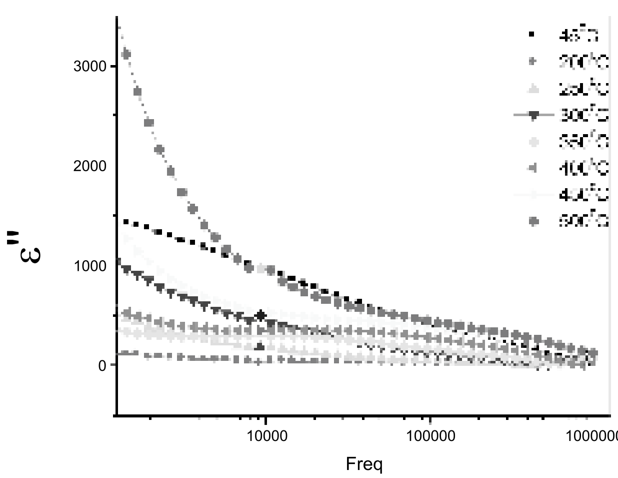


**Fig. 8. Variation of dielectric constant with temperature at different frequencies.**

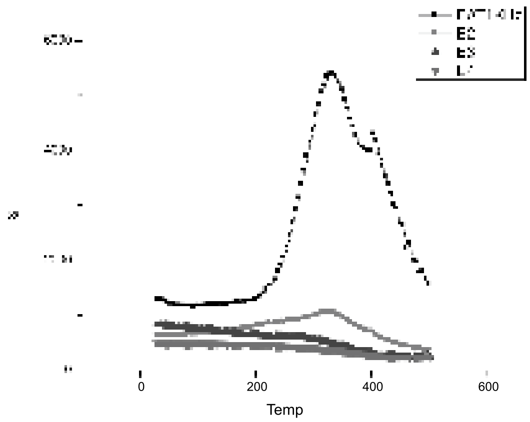


**Fig. 9. Variation of dielectric loss with frequency at different temperatures**

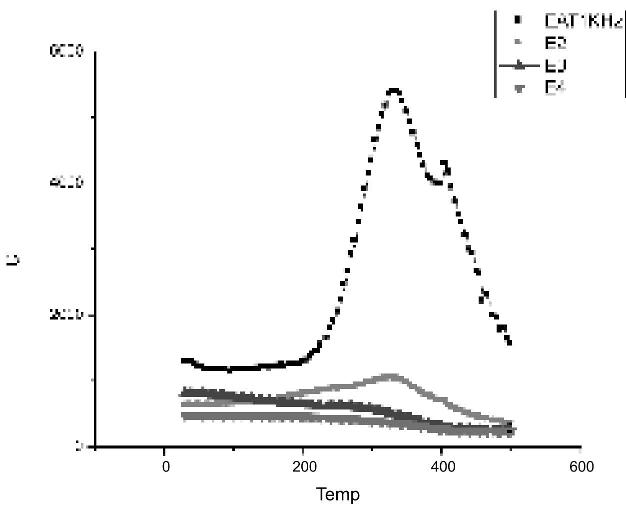


**Fig. 10. Variation of dielectric loss with temperature at different frequencies**

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